

Bldg 3<sup>8</sup> Floor**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 22, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

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GROUP 1105

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AMENDMENT AFTER FINAL REJECTION**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

Claims 112, 113, 117, 118, 122, and 123 have been rejected under 35 USC 112 as indefinite for using the terminology "layer-type". Applicants respectfully disagree.

The undersigned attorney did a search in Lexis for the terms "layer-type" and the term "layer" preceding the term "type" by one word (layer pre/1 type). In this search Lexis found 225 issued US patents using this terminology in the claims. The USPTO has, therefore, accepted this terminology as definite within the meaning of 35 USC 112. Attachment A is the results of this search printed out using the .kw or "kwick" feature which prints the searched terms and words before and after the searched term. The searched terminology appears in a number of forms such as "layer type", "layer-type",

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To Barbara Thomas  
From Dan Morris

12/22/98

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Sir:

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"layer of type". In view thereof applicants respectfully request the examiner to withdraw the rejection of claims 112, 113, 117, 118, 122, and 123 under 35 USC 112 as indefinite for using the terminology "layer-type".

In Attachment B there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "Layered like" and "layered type" in on-line non-patent literature prior to applicants' filing date. From Attachment B it is clear that these terms are used and understood by persons of skill in the art.

In Attachment C there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "rare earth like" in on-line non-patent literature prior to applicants' filing date. From Attachment C it is clear that this term is used and understood by persons of skill in the art. This is in addition to previously submitted evidence of the definiteness of this term to overcome the rejection of applicants claims as indefinite for using the term "rare earth like" which applicants respectfully request the examiner to withdraw.

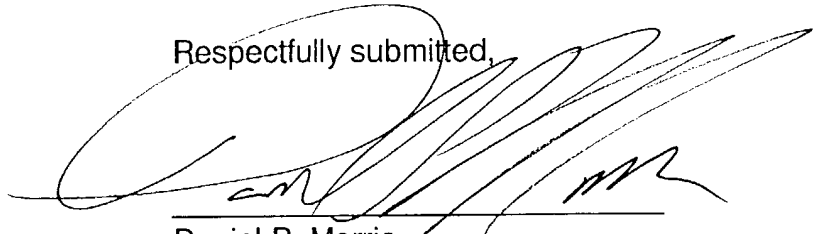
In Attachment D there is a search done by Jim Leonard, an IBM Research librarian, at the request of the undersigned attorney of the term "perovskite like" in on-line non-patent literature prior to applicants' filing date. From Attachment D it is clear that this term is used and understood by persons of skill in the art. This is in addition to previously submitted evidence of the definiteness of this term to overcome the rejection

of applicants claims as indefinite for using the term "perovskite like" which applicants respectfully request the examiner to withdraw.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

A handwritten signature in black ink, appearing to be "Daniel P. Morris", written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

ATTACHMENT A

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Tue, 22 Dec 1998 12:45:14 -0500  
Message-Id: <199812221745.AA26465@prod.lexis-nexis.com>  
Received: by prod.lexis-nexis.com (Internal Mail Agent-1);  
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CLAIMS(LAYER-TYPE OR (LAYER PRE/1 TYPE))

NUMBER OF PATENTS FOUND WITH YOUR REQUEST THROUGH:  
LEVEL 1... 225

LEVEL 1 PRINTED

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\*\*\*\*\*02438\*\*\*\*\*

PAGE 1

LEVEL 1 - 1 OF 225 PATENTS

5,828,093

Oct. 27, 1998

Ceramic capacitor and semiconductor device in which the ceramic capacitor is mounted

INVENTOR: Naito, Yasuyuki, Kyoto, Japan  
Sakabe, Yukio, Kyoto, Japan

... [\*1] by a gap and surrounding said first capacitor electrode.

[\*2] 2. A ceramic capacitor according to claim 1, wherein said ceramic dielectric substrate comprises a substrate for an SrTiO<sub>3</sub> boundary layer type semiconductive capacitor.

[\*3] 3. A ceramic capacitor according to claim 1, further comprising outer electrodes which are mainly made of at least one material selected from the group consisting of Au, Pt and Pd and formed on at ...

... [\*12] layer is formed on said second principal face of said substrate.

[\*13] 13. A ceramic capacitor according to claim 5, wherein said ceramic dielectric substrate comprises a substrate for an SrTiO<sub>3</sub> boundary layer type semiconductive capacitor.

[\*14] 14. A ceramic capacitor according to claim 5, wherein said first capacitor electrode formed on said first principal face of said ceramic substrate is divided into two parts.

[\*15] 15. ...

... [\*19] layers disposed respectively on said first and second capacitor electrodes.

[\*20] 20. A ceramic capacitor according to claim 19, wherein said ceramic dielectric substrate comprises a substrate for an SrTiO<sub>3</sub> boundary layer type semiconductive capacitor.

[\*21] 21. A ceramic capacitor according to claim 20, further comprising outer electrodes which are mainly made of at least one material selected from the group consisting of Au, Pt and Pd and formed on at ...

... [\*25] layer formed on said first principal face of said substrate.

[\*26] 26. A ceramic capacitor according to claim 23, wherein said ceramic dielectric substrate comprises a substrate for an SrTiO<sub>3</sub> boundary layer type semiconductive capacitor.

[\*27] 27. A ceramic capacitor according to claim 23, wherein said first capacitor electrode formed on said first principal face of said ceramic

substrate is divided into two parts.

Pat. No. 5828093, \*27

PAGE 2

[\*28] 28. ...

LEVEL 1 - 2 OF 225 PATENTS

PAGE 3

5,793,767

<=2> GET 1st DRAWING SHEET OF 21

Aug. 11, 1998

ATM communication device and ATM communication network  
system with terminal devices having uniquely assigned  
virtual channel identifiers

INVENTOR: Soda, Keiichi, Kanagawa, Japan  
Ichihashi, Tatsuki, Kanagawa, Japan  
Ushisako, Yukio, Kanagawa, Japan  
Kashima, Kazuyuki, Kanagawa, Japan  
Yokotani, Tetsuya, Kanagawa, Japan  
Hiramatsu, Koichi, Kanagawa, Japan  
Shibahara, Makoto, Hyogo, Japan

... [\*6] ATM cell transmission section of the first ATM terminal  
communication device to the other ATM terminal communication devices is stored  
into a segmentation and reassemble sublayer protocol data unit for an ATM  
adaptation layer type 3 or 4 in addition to the field of the virtual path  
identifier and the virtual channel identifier in the first ATM cell.

[\*7] 7. The ATM communication network system of claim 6, wherein the  
segmentation and reassemble sublayer ...

... [\*8] cell transmission section of the first ATM terminal communication  
device to the other ATM terminal communication devices is stored into a common  
part convergence sublayer protocol data unit for an ATM adaptation layer type 3  
or 4 in addition to the field of the virtual path identifier and the virtual  
channel identifier in the first ATM cell.

[\*9] 9. The ATM communication network system of claim 8, wherein the common  
part convergence ...

... [\*10] space to be changed and transmitted from the ATM cell  
transmission section to the other ATM terminal communication devices is stored  
into a common part convergence sublayer protocol data unit for an ATM adaptation  
layer type 5 in addition to the field of the virtual path identifier and the  
virtual channel identifier in the first ATM cell.

[\*11] 11. The ATM communication network system of claim 10, wherein the  
common part convergence sublayer ...

LEVEL 1 - 3 OF 225 PATENTS

PAGE 4

5,774,665

<=2> GET 1st DRAWING SHEET OF 6

Jun. 30, 1998

Asynchronous transfer mode LAN switching hub device using  
IEEE P1355 standard and its control method

INVENTOR: Jeong, Seong-Ho, Yusong-ku, Republic of Korea  
Kim, Jang-Kyung, Yusong-ku, Republic of Korea  
Chong, Il-Young, Seo-ku, Republic of Korea

... [\*3] said ATM-to-P1355 module includes: a PHY layer having an ATM physical layer for directly connecting with the ATM network, an ATM layer for executing ATM protocol, an AAL (ATM Adaptation Layer) type layer for executing an ATM adaptable function, a LAN emulation layer for executing LAN emulation function, a bridging/relay layer for executing a bridging and relay function, an ...

PAGE 5

LEVEL 1 - 4 OF 225 PATENTS

5,764,658

<=2> GET 1st DRAWING SHEET OF 36

Jun. 9, 1998

Data receiving apparatus and method

INVENTOR: Sekiguchi, Shun-ichi, Kanagawa, Japan  
Murakami, Tokumichi, Kanagawa, Japan  
Kato, Yoshiaki, Kanagawa, Japan

... [\*1] bit stream of data blocks, each comprising a digital coded bit sequence, which are organized in a hierarchy including a plurality of layers, each layer having associated therewith one of a plurality of layer types, wherein at least one layer of a high-order layer type is composed of at least one layer of a lower-order layer type, each of the data blocks corresponding to one of the layers and including a start code which identifies the layer type of the data block, the apparatus comprising:

a layer memory for storing data indicating the layer type corresponding to the last start code received in the bit stream, the layer memory having a last layer type output,

a first expected start code selector coupled to receive the last layer type output from the layer memory, the first expected start code selector selecting and generating a first expected start code selector output identifying a set of expected start codes based on the last layer type received, wherein start codes of data blocks in the high-order layers are identified as expected start codes before start codes of data blocks in the lower-order layers;



start code ...

... [\*1] detected start code, if one of the expected start codes is similar to data in the bit stream, the start code detector having a start code detector output which identifies the detected start code and its corresponding layer type;

means responsive to the start code detector output for updating the layer memory with data indicating the layer type corresponding to the detected start code; and

a block data decoder, responsive to the detected start code output from the start code detector, for decoding the data block corresponding to the detected start code.

[\*2] 2. An ...

... [\*12] bit stream of data blocks, each comprising a digital coded bit sequence, which are organized in a hierarchy including a plurality of layers, each layer having associated therewith one of a plurality of layer types, wherein at least one layer of a high-order layer type is composed of at least one layer of a lower-order layer type, each of the data blocks corresponding to one of the layers and including a start code which identifies the layer of the data block, the method comprising the steps of:

Pat. No. 5764658, \*12

PAGE 6

storing data indicating the layer corresponding to the last start code ...

... [\*12] a set of expected start codes based upon the data indicating the layer wherein said set of expected start codes lists start codes of data blocks in layers of said high-order layer type before start codes of data blocks in layers of said lower-order layer type;

continuously comparing data in the bit stream with the set of expected start codes;

selecting one of the expected start codes as a detected start code based on the comparison, if one of the expected start ...

LEVEL 1 - 5 OF 225 PATENTS

5,720,851

<=2> GET 1st DRAWING SHEET OF 2

Feb. 24, 1998

Method and arrangement for producing a foam-formed fibre or paper web

INVENTOR: Reiner, Lennart, Matfors, Sweden

... [\*11] plurality of dispersion vessels.

PAGE 7

[\*12] 12. Arrangement according to claim 11, wherein the different fibre types are metered separately from the dispersion vessels up to an inlet box of the paper machine, said inlet box being of multi-layer type.

[\*13] 13. Method according to claim 1, wherein the foam-formed fibre web includes a paper web.

[\*14] 14. Method according to claim 1, wherein the foamed fibre dispersion is formed by dispersing natural ...

LEVEL 1 - 6 OF 225 PATENTS

5,715,250

<=2> GET 1st DRAWING SHEET OF 4

Feb. 3, 1998

ATM-lan connection apparatus of a small scale capable of connecting terminals of different protocol standards and ATM-lan including the ATM-lan connection apparatus

INVENTOR: Watanabe, Ayumi, Tokyo, Japan

... [\*1] first ATM terminal for receiving as a first reception cell a first ATM cell supplied from said first ATM terminal;

a first AAL5-SAR (ATM Adaptation Layer type 5-Segmentation And Reassembly) section for reassembling said first reception cell into a first AAL5 packet to output said first AAL5 packet as a first LAN emulation frame;

...

... [\*3] first ATM terminal for receiving as a first reception cell a first ATM cell supplied from said first ATM terminal;

a first AAL5-SAR (ATM Adaptation Layer type 5-Segmentation And Reassembly) section for reassembling said first reception cell into a first AAL5 packet to output said first AAL5 packet as a first LAN emulation frame;

...

LEVEL 1 - 7 OF 225 PATENTS

5,714,403

<=2> GET 1st DRAWING SHEET OF 3

Feb. 3, 1998

Process for producing a matrix of "all optical" vertically-structured quantum well components

INVENTOR: Nissim, Yves, Paris, France  
Bensoussan, Marcel, Boulogne, France  
Oudar, Jean-Louis, Chatenay Malabry, France  
Rao, Elchuri, Issy Les Moulineaux, France

... [\*2] in that the quantum well layer is a binary, ternary or quaternary GaAs or InP-based III-V semiconductor.

[\*3] 3. A process according to claim 2, characterized in that the quantum well active layer is of the type GaAs/Ga[1-x]Al[x]As with  $0 < x < 1$ , or GaAs/Ga[1-x]In[x]As with  $0 < x < 1$  or InP/In[x]Ga[1- ...

... [\*3] In[x]Ga[1-x]As[y]P[1-y] with  $0 < x < 1$  and with  $0 < y < 1$ .

[\*4] 4. A process according to claim 1, characterized in that the positive layer is of type Si[x]N[y] or possibly SiO[x]N[y], with y, in the latter case, being small enough to enable the SiO[x]N[y] based layer to behave as a positive layer.

[\*5] 5. A process according to claim 1, characterized in that the negative layer is of type Si[x]N[y] or possibly SiO[x]N[y], with y being small enough to enable the SiO[x]N[y] based layer to behave as a negative layer.

[\*6] ...

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LEVEL 1 - 8 OF 225 PATENTS

5,702,792

<=2> GET 1st DRAWING SHEET OF 8

Dec. 30, 1997

Optical recording medium

INVENTOR: Iida, Tetsuya, Tsurugashima, Japan  
Jinno, Satoshi, Tsurugashima, Japan  
Higuchi, Takanobu, Tsurugashima, Japan

What is claimed is:

[\*1] 1. An optical recording medium of a multi-layer type comprising:

a substrate

a single or plural spacer layers each carrying pits and/or grooves;

a single or plural reflective layers layered on the spacer layers; and

wherein said reflective layer is made of a ...

... [\*1] OH groups and a surface of said reflecting layer furthest from said substrate contacting with said spacer layer is provided with a silane coupling treatment.

[\*2] 2. An optical recording medium of a multi-layer type comprising:

a substrate

a single or plural spacer layers each carrying pits and/or grooves;

a single or plural reflective layers layered on the spacer layers; and

wherein said reflective layer is made of one or ...

LEVEL 1 - 9 OF 225 PATENTS

5,693,085

<=2> GET 1st DRAWING SHEET OF 6

Dec. 2, 1997

Stent with collagen

INVENTOR: Buirge, Andrew W., Minneapaulis, Minnesota  
Buscemi, Paul J., Long Lake, Minnesota  
Burmeister, Paul H., Maple Grove, Minnesota

... [\*21] combination of claim 20 wherein the collagen material includes Type I and Type IV layers.

[\*22] 22. The combination of claim 21 wherein the Type IV is SIS.

[\*23] 23. The combination of claim 22 wherein the Type IV is the innermost layer and the Type I layer includes a drug.

[\*24] 24. The combination of claim 17 wherein the stent is of variable diameter.

[\*25] 25. The combination of claim 24 wherein the stent is of the self-expanding type.

[\*26] 26. The combination of claim 17 wherein the liner has ...

PAGE 12

LEVEL 1 - 10 OF 225 PATENTS

5,668,353

<=2> GET 1st DRAWING SHEET OF 7

Sep. 16, 1997

Input panel avoiding interference pattern and method of forming the same

INVENTOR: Matsuda, Genichi, Kawasaki, Japan  
Tanaka, Toshiaki, Kawasaki, Japan

What is claimed is:

[\*1] 1. An input panel of a resistance layer type comprising:  
a first board having a first transparent conductive layer on one surface;  
a second board having a second transparent conductive layer on one surface,  
said first board and said ...  
... [\*3] as claimed in claim 1, wherein said second spacers are arranged at intervals from 0.5 mm to 20 mm, and said first spacers are arranged at smaller intervals.

[\*4] 4. An input panel of a resistance layer type comprising:  
a first board having a first transparent conductive layer on one surface;  
a second board having a second transparent conductive layer on one surface,  
said first board and said ...

... [\*4] first spacers have such a height smaller than that of said second spacers that an appropriate input sensitivity of said input panel can be achieved.

[\*5] 5. A method of forming an input panel of a resistance layer type, said method comprising the steps of:

a) forming first spacers on a first transparent conductive layer formed on a first board, said first spacers being non-conductive and having a height ...

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LEVEL 1 - 11 OF 225 PATENTS

5,665,502

<=2> GET 1st DRAWING SHEET OF 1

Sep. 9, 1997

Electrophotographic photoreceptor and method for producing the photoreceptor

INVENTOR: Ohashi, Kunio, Nara, Japan  
Tokuyama, Mitsuru, Nara, Japan  
Kinashi, Hiroshi, Kyoto, Japan  
Nozomi, Mamoru, Kanagawa, Japan

Umehara, Tadashi, Niigata, Japan  
Asari, Toshiya, Kanagawa, Japan

... [\*8] a developing gap holding jig, and in a region in contact with a cleaner.

[\*9] 9. An electrophotographic photoreceptor as claimed in claim 1, wherein said photoconductive layer is a laminated layer type photoconductive layer comprising at least a charge generating layer and a charge transfer layer, said charge generating layer having a thickness of from 0.1 to 2  $\mu$ m, and said charge transfer ...

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LEVEL 1 - 12 OF 225 PATENTS

5,647,284

<=2> GET 1st DRAWING SHEET OF 6

Jul. 15, 1997

Method and apparatus for shipping knobbed glass cookware covers

INVENTOR: Frysinger, Eric T., Groveport, Ohio  
Pirello, Joe, Reynoldsburg, Ohio

... [\*3] layer of said type of goods may be placed, the partition further including a plurality of integrally-formed flaps, each flap assuming an upwardly-angled position when one of said projections from a layer of such type of goods stacked immediately underneath the partition projects upward through an opening in the partition formed by said flap,

(c) a substantially rigid top plate for covering a top layer of said type of goods, the plate having a size and shape approximately equal to that of said pallet and including a plurality of equally-spaced holes to accommodate said projections from said top layer of such type of goods when said goods are stacked on a partition there beneath, said top plate further including substantially square notches inwardly-formed into its corners to complementarily engage vertical corner posts on said pallet so ...

LEVEL 1 - 13 OF 225 PATENTS

5,642,188

<=2> GET 1st DRAWING SHEET OF 2

Jun. 24, 1997

Wet-type electrophotographic image formation method

INVENTOR: Mochizuki, Manabu, Yokohama, Japan  
Kurotori, Tsuneo, Tokyo, Japan  
Ariyama, Kenzo, Yokohama, Japan  
Kojima, Kenji, Tokyo, Japan

PAGE 15

Tsuruoka, Ichiro, Tokyo, Japan  
Echigo, Katsuhiro, Yokohama, Japan  
Miyao, Mayumi, Tokyo, Japan

... [\*1] said silicone oil, and said photoconductive member is an organic photoconductive member.

[\*2] 2. The wet-type image formation apparatus as claimed in claim 1, wherein said organic photoconductor is of a single layer type in which a charge generating material and a charge transporting material are contained.

[\*3] 3. The wet-type image formation apparatus as claimed in claim 1, wherein said photoconductive layer comprises ( ...

... [\*9] said silicone oil, and said photoconductive member is an organic photoconductive member.

[\*10] 10. The wet-type image formation apparatus as claimed in claim 9, wherein said organic photoconductor is of a single layer type in which a charge generating material and a charge transporting material are contained.

[\*11] 11. The wet-type image formation apparatus as claimed in claim 9, wherein said photoconductive layer comprises ( ...  
LEVEL 1 - 14 OF 225 PATENTS

5,636,097

<=2> GET 1st DRAWING SHEET OF 3

Jun. 3, 1997

Protective circuit for semiconductor power device

INVENTOR: Palara, Sergio, Catania, Italy  
Sueri, Stefano, Catania, Italy

... [\*1] second circuit means comprise a condenser in an N + /P junction located in an epitaxial region contained within an insulation well of the type P in turn contained in an epitaxial layer of the type N - grown on a substrate of the type N + , and an NPN transistor having as the collector an enriched region of the type n + of said epitaxial region, as the base said insulation well of the type P and as the ...

... [\*7] second circuit means comprise a condenser in an N + /P junction located in an epitaxial region contained within an insulation well of the type P in turn contained in an epitaxial layer of the type N-grown on a substrate of the type N + , and an NPN transistor having as the collector an enriched region of the type n + of said epitaxial region, as the base said insulation well of the type P and as the ...

LEVEL 1 - 15 OF 225 PATENTS

5,623,181

Apr. 22, 1997

Multi-layer type light emitting device

INVENTOR: Suehiro, Yoshinobu, Gyoda, Japan  
Yamazaki, Shigeru, Gyoda, Japan  
Sato, Takashi, Gyoda, Japan

What is claimed is:

[\*1] 1. A multi-layer type light emitting device, comprising:

at least two light emitting sources, successively disposed along a light-transmitting path, including a rearmost source at a rear end of the path and a ...

... [\*1] direction rays of light emitted by each source except the rearmost source, and for transmitting therethrough in the forward direction rays of light emitted by the rearmost source.

[\*2] 2. A multi-layer type light emitting device according to claim 1, which further comprises a reflection surface disposed so as to correspond to said rearmost light emitting source, for reflecting rays of light emitted by said rearmost light emitting source and radiating the rays of light in the forward direction.

[\*3] 3. A multi-layer type light emitting device according to claim 1, wherein said light emitting sources emit rays of light with different luminous wavelength ranges, respectively.

[\*4] 4. A multi-layer type light emitting device according to claim 3, wherein said light emitting sources include ones emitting rays of red or nearly red light, green or nearly green light and blue or nearly blue light respectively.

[\*5] 5. A multi-layer type light emitting device according to claim 1, wherein at least one of said light emitting sources emits ray of light with two or more luminous wavelength ranges.

[\*6] 6. A multi-layer type light emitting device according to claim 1, wherein said at least two light emitting sources includes three light emitting sources, and wherein the respective optical surface for each light emitting source except the rearmost source each reflects rays of light emitted by said light emitting source with approximately the same luminous intensity distribution characteristics.

[\*7] 7. A multi-layer type light emitting device according to claim 1, wherein said optical surface is a light semi-transmissible thin film reflection surface, or said optical surface is formed by a method wherein reflection



portions are partially formed on a light transmissible surface.

18

Pat. No. 5623181, \*7

[\*8] 8. A multi-layer type light emitting device according to claim 1, wherein said optical surface is a wavelength selective surface.

[\*9] 9. A multi-layer type light emitting device according to claim 8, wherein said optical surface is a dichroic mirror formed by multi-layering of thin films having different refractive indexes.

[\*10] 10. A multi-layer ...

... [\*10] each of said optical surface and said reflection surface of each of said sources is a concave surface facing a luminous surface of said at least one LED chip.

[\*11] 11. A multi-layer type light emitting device according to claim 10, wherein the respective optical surface and said LED chip of each source, except the rearmost source, and said reflection surface and said LED chip are each integrally formed of a first light transmissible material, thereby forming respective LEDs.

[\*12] 12. A multi-layer type light emitting device according to claim 11, wherein each LED is disposed in such a manner that a front surface thereof is complementary to and closely connected with a rear surface of an LED of a source positioned forward thereof.

[\*13] 13. A multi-layer type emitting device according to claim 11, further comprising a second light transmissible material having a refractive index approximately the same as that of the first light transmissible material filling a space ...

... [\*15] surface or said reflection surface for the source having the LED chip, and

wherein said optical surface is formed on a front surface of the light transmissible material sealing the LED of the rearmost source.

[\*16] 16. A multi-layer type light emitting device according to claim 11, wherein an incident surface is provided on the path rearward of each optical surface, in spaced relation thereto, further comprising a further light transmissible material filling ...

... [\*16] optical surface, wherein rays of light emitted on the path rearward of the incident surface in the forward direction pass through the incident surface, the further light transmissible material and the optical surface.

[\*17] 17. A multi-layer type light emitting device according to claim 1, wherein the at least two light emitting sources includes at least three light

emitting sources, successively disposed along the light-transmitting path, the at least three ...

... [\*17] source, each optical surface transmitting therethrough in the forward direction rays of light emitted by each rear source that is disposed between the optical surface and the rear end.

Pat. No. 5623181, \*17

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[\*18] 18. A multi-layer type light emitting device, comprising:

at least two light emitting sources, successively disposed along a light-transmitting path, including a rearmost source at a rear end of the path and a ...

... [\*18] transmitting therethrough in the forward direction rays of light emitted by the rearmost source;

wherein each of the light emitting sources, except the rearmost source, is a semiconductor LED chip.

[\*19] 19. A multi-layer type light emitting device according to claim 18, wherein the at least two light emitting sources includes at least three light emitting sources, successively disposed along the light-transmitting path, the at least three ...

... [\*19] source, each optical surface transmitting therethrough in the forward direction rays of light emitted by each rear source that is disposed between the optical surface and the rear end.

[\*20] 20. A multi-layer type light emitting device, comprising:

at least two light emitting sources, successively disposed along a light-transmitting path, including a rearmost source at a rear end of the path and a ...

... [\*20] flat optical board formed of a light transmissible material, the light transmissible material having an annular optical surface surrounding a side surface of the at least one LED chip.

[\*21] 21. A multi-layer type light emitting device according to claim 20, wherein the at least two light emitting sources includes at least three light emitting sources, successively disposed along the light-transmitting path, the at least three ...

LEVEL 1 - 16 OF 225 PATENTS

PAGE 20

5,605,051

<=2> GET 1st DRAWING SHEET OF 83

Feb. 25, 1997

Automotive air conditioner having condenser and evaporator  
provided within air duct

INVENTOR: Iritani, Kunio, Anjo, Japan  
Numazawa, Shigeo, Nagoya, Japan  
Fujiwara, Kenichi, Kariya, Japan  
Yamanaka, Yasushi, Nakashima-gun, Japan  
Isaji, Akira, Nishio, Japan  
Suzuki, Takahisa, Kariya, Japan  
Sanada, Ryoichi, Kariya, Japan

... [\*13] converting a variation of temperature of the refrigerant flowing  
from said condenser into a variation of pressure.

[\*14] 14. An automotive air conditioner according to claim 13, wherein said  
condenser and said subcooler are formed as one layer type heat exchanger having  
a large number of tubes serving as refrigerant passageway, a large number of  
heat radiating fins layered alternately with the tubes, and a pair of headers  
disposed on the opposite ends of the tubes.

[\*15] 15. An automotive air conditioner according to claim 14, wherein said  
layer type heat exchanger comprises a partition plates in said headers in order  
that refrigerant flow is turned back and a mounting pipe for mounting said  
temperature sensitive tube.

[\*16] 16. An ...

LEVEL 1 - 17 OF 225 PATENTS

5,589,960

<=2> GET 1st DRAWING SHEET OF 4

Dec. 31, 1996

Liquid crystal display system

INVENTOR: Chiba, Masao, Saitama, Japan  
Ishii, Mikio, Saitama, Japan

What is claimed is:

[\*1] 1. A double-layer type super-twisted nematic liquid crystal display  
system comprising:

a dot-matrix type liquid crystal display device for displaying at least one  
of characters and graphic forms;

a compensating ...

... [\*1] crystal display device and said compensating liquid crystal device are driven with said drive voltages which are adjusted according to the calculation of contrast made with the aid of said light detecting means.

[\*2] 2. A double-layer type super twisted nematic liquid crystal display system according to claim 1, further comprising:

a voltage memory circuit for storing most recent values of said drive voltages while said system is an off state to provide initial drive voltage values for when said system is switched to an on state.

[\*3] 3. A double-layer type super-twisted nematic liquid crystal display system comprising:

a dot-matrix type liquid crystal display device for displaying at least one of characters and graphic forms;

a compensating ...

... [\*3] said light detecting means and said liquid crystal display has a luminance measuring region which is turned on and off for measurement of the contrast of said liquid crystal display device.

[\*4] 4. A double layer type super-twisted nematic liquid crystal display system comprising:

a dot-matrix type liquid crystal display device for displaying at least one of characters and graphic forms;

a compensating ...

... [\*4] liquid crystal display device has a luminance measuring region which is divided into two parts which are alternately turned on and off for measurement of the contrast of said liquid crystal display device.

AGE 22

Pat. No. 5589960, \*4

[\*5] 5. A double layer type super-twisted nematic liquid crystal display system comprising:

a dot-matrix type liquid crystal display device for displaying at least one of characters and graphic forms;

a compensating ...

LEVEL 1 - 18 OF 225 PATENTS

5,580,816

<=2> GET 1st DRAWING SHEET OF 5

Dec. 3, 1996

Local oxidation process for high field threshold applications

INVENTOR: Hemmenway, Donald F., Melbourne, Florida  
Pearce, Lawrence G., Palm Bay, Florida

... [\*1] another;

providing an implant of a dopant species in a defined field region adjacent two of the device regions, said implant of sufficient energy and concentration to impart nucleation sites within the device layer of the type known to result in stacking faults during oxide growth conditions;

providing a thickness of thermally grown silicon dioxide in the field regions by thermally processing the structure to remove nucleation ...

PAGE

24

LEVEL 1 - 19 OF 225 PATENTS

5,575,418

<=2> GET 1st DRAWING SHEET OF 12

Nov. 19, 1996

Corrugated paperboard package systems with gas-permeable plastic membranes for modified atmosphere packaging of fresh fruits and vegetables and cut flowers

INVENTOR: Wu, Chiu H., Vancouver, Canada  
Oikarinen, Juhani I., Lahti, Finland  
Matstoms, Bo, Orebro, Sweden  
Powrie, William D., North Vancouver, Canada

... [\*9] paperboard combination so that no natural pinholes are formed.

[\*10] 10. A paperboard as claimed in claim 1 wherein the overall permeability of the paperboard combination is regulated in part by regulating the composition of the polymer layer and the type of kraft paper.

[\*11] 11. A paperboard as claimed in claim 1 wherein the polymer is selected from the group consisting of ethylene vinylacetate (EVA), ethylbutyl acetate (EBA), a crosslinked ionomer resin, cast ...

LEVEL 1 - 20 OF 225 PATENTS

PAGE 25

5,570,084

<=2> GET 1st DRAWING SHEET OF 7

Oct. 29, 1996

Method of loose source routing over disparate network types in a packet communication network

INVENTOR: Ritter, Michael W., Los Altos, California  
Bettendorff, John, San Jose, California  
Flammer, III, George H., Cupertino, California  
Galloway, Brett D., Campbell, California

What is claimed is:

- [\*1] 1. A method for digital packet communication between nodes in disparate networks including path unaware network layer types and path aware network layer types, said method comprising:
- a) receiving a typed encapsulating packet which encapsulates a path-addressed packet at a first network layer, said first network layer being path aware;
- ...
- ... [\*1] path aware protocol if said second network layer is path aware.
- [\*2] 2. A method for digital packet communication between nodes in disparate networks including path unaware network layer types and path aware network layer types, said method comprising:
- a) receiving an encapsulating packet which encapsulates a path-addressed packet at a first network layer of a first type;
  - b) if said first type is path unaware, ...
- ... [\*6] type of the received packet; and
- relaying the received packet to an appropriate network router.
- [\*7] 7. A method for digital packet communication between nodes in various networks including path aware network layer types, said method comprising:
- a) designating a destination path element for a packet by means of a type-length-value element specific only to one station of a group of ...

PAGE 26

LEVEL 1 - 21 OF 225 PATENTS

5,555,347

<=2> GET 1st DRAWING SHEET OF 24

Sep. 10, 1996

Method and apparatus for controlling a robot using a neural network

INVENTOR: Yoneda, Takao, Nagoya, Japan  
Komura, Katsuhiro, Takahama, Japan

... [\*2] accordance with the second joint angle vector calculated by said second calculation means.

[\*3] 3. An apparatus for controlling an articulated robot according to claim 2, wherein said neural network is of a three layer type which is composed of an input layer, an intermediate layer and an output layer.

[\*4] 4. An apparatus for controlling an articulated robot according to claim 2, further comprising:

actual position measurement means for measuring the actual ...

GE 27

LEVEL 1 - 22 OF 225 PATENTS

5,545,945

<=2> GET 1st DRAWING SHEET OF 1

Aug. 13, 1996

Thermionic cathode

INVENTOR: Branovich, Louis E., Howell, New Jersey  
Eckart, Donald W., Wall, New Jersey  
Fischer, Paul, Oakhurst, New Jersey

... [\*2] emissions.

[\*3] 3. A thermionic cathode as recited in claim 2 wherein the cathode is an impregnant-type cathode.

[\*4] 4. A thermionic cathode as recited in claim 2 wherein the cathode is a layer-type cathode.

[\*5] 5. An enhanced electron emission thermionic cathode, comprising:

a base material having a composition including Barium and Tungsten; and

an overcoating of emissive material forming an emissive surface on said base material;

...

LEVEL 1 - 23 OF 225 PATENTS

5,525,541

<=2> GET 1st DRAWING SHEET OF 6

Jun. 11, 1996

Method of making an electronic and/or photonic component

INVENTOR: Krauz, Philippe, Creteil, France  
Rao, Elchuri K., Issy-Les-Moulineaux, France

... [\*1] region of the quantum well layer on which the dielectric layer is deposited to confer on said region electro-optical or photonic properties that correspond to said function.

[\*2] 2. A method according to claim 1, wherein the quantum well layer is of the type based on GaAs and on InP.

[\*3] 3. A method according to claim 2, wherein the quantum well layer is of one of the following types: GaAs/GaAlAs; InGaAs/Ga(Al)As; InGaAs/InAlAs; InGaAs/InP; and ...

PAGE 29

LEVEL 1 - 24 OF 225 PATENTS

5,504,558

<=2> GET 1st DRAWING SHEET OF 1

Apr. 2, 1996

Electrophotographic photosensitive member, and  
electrophotographic apparatus and device unit employing the  
same

INVENTOR: Ikezue, Tatsuya, Yokohama, Japan

... [\*11] photosensitive member according to claim 10, wherein the charge-transporting layer has a thickness of from 15 to 30  $\mu$ m.

[\*12] 12. An electrophotographic photosensitive member according to claim 1, wherein the photosensitive layer is of a single layer type.

[\*13] 13. An electrophotographic photosensitive member according to claim 12, wherein the photosensitive layer has a thickness of from 10 to 35  $\mu$ m.

[\*14] 14. An electrophotographic photosensitive member according to claim 13, wherein the photosensitive layer has a ...

LEVEL 1 - 25 OF 225 PATENTS

PAGE 30

5,489,372

Feb. 6, 1996

Process for producing light absorption layer of solar cell

INVENTOR: Hirano, Tomio, Susono, Japan



... [\*7] indium plating bath with a dispersion of fine particles of selenium suspended therein to form a multi-layer electrodeposited layer including copper, indium, and selenium on said conductive substrate; and

heat-treating the multi-layer type electrodeposition layer to convert it into a ternary alloy layer of copper-indium-selenium.

[\*8] 8. The process according to claim 7, wherein said copper plating bath is a sulfuric acid type electrodeposition bath which ...

LEVEL 1 - 26 OF 225 PATENTS

5,475,700

<=2> GET 1st DRAWING SHEET OF 5

Dec. 12, 1995

Laser diode with electron and hole confinement and barrier layers

INVENTOR: Iwata, Hiroshi, Tokyo, Japan

... [\*11] indices of said hole confinement layer and said electron confinement layer.

[\*12] 12. A laser diode as claimed in claim 11, wherein said hole confinement layer and said electron confinement layer are type II compound layers.

[\*13] 13. A laser diode as claimed in claim 11, wherein said hole confinement layer and said electron confinement layer are type II superlattice layers.

[\*14] 14. A laser diode as claimed in claim 11, wherein said hole potential in said hole confinement layer increases with distance away from said interface with ...

LEVEL 1 - 27 OF 225 PATENTS

5,466,892

<=2> GET 1st DRAWING SHEET OF 3

Nov. 14, 1995

Circuit boards including capacitive coupling for signal transmission and methods of use and manufacture

INVENTOR: Howard, James R., Santa Clara, California  
Lucas, Gregory L., Newark, California

... [\*3] between sets of the additional signal and receptor pads on the first and second conductive layers also for electrostatic transmission of AC signals therebetween.

[\*4] 4. The circuit board of claim 1 wherein the circuit board is of a multi-layer type having at least a third conductive layer and further wherein the additional conductive circuit means on the adjacent pairs of the first, second and third conductive layers form additional signal and receptor pads separated by additional ...

... [\*9] coupling between sets of the additional signal and receptor pads on the first and second conductive layers also for electrostatic transmission of AC signals therebetween.

[\*10] 10. The method of claim 7 wherein the circuit board is of a multi-layer type having at least a third conductive layer and further wherein the additional conductive circuit means on the adjacent pairs of the first, second and third conductive layers form additional signal and receptor pads separated by additional ...

... [\*13] in the AC signal transmitting circuit whereby capacitive reactance and inductive reactance approach equality in order to optimize capacitive coupling.

[\*14] 14. The circuit board of claim 13 wherein the circuit board is of a multi-layer type having at least a third conductive layer and further wherein the additional conductive circuit means on the adjacent pairs of the first, second and third conductive layers form additional signal and receptor means separated by additional ...

LEVEL 1 - 28 OF 225 PATENTS

5,466,609

<=2> GET 1st DRAWING SHEET OF 5

Nov. 14, 1995

Biodegradable gelatin-aminodextran particle coatings of and processes for making same

INVENTOR: Siiman, Olavi, Davie, Florida  
Burshteyn, Alexander, Hialeah, Florida  
Gupta, Ravinder K., Pembroke Pines, Florida

CORE TERMS: gelatin, magnetic, particle, antibody, aminodextran, cell, bead, sample, ferrite, coating, minute, suspension, depletion, coated, tube, biological, rbc, crosslinked, sulphydryl, mixed, conjugated, aqueous, layer, crosslinking, granulocyte, maleimidy, preparation, wbc, dextran, manganese

We claim:

[\*1] 1. Colloidal particles having a plurality of pendent functional groups on an exterior coating of aminodextran in which each particle comprises a solid metallic core coated with a first gelatin layer of type B, alkali cured gelatin of Bloom in the range 60 to 225 and a second layer of an aminodextran, said layers having been either (a) crosslinked by the action of a chemical crosslinking agent or (b) ...

... [\*16] preparing discrete colloidal particles having a plurality of pendent functional groups on an exterior coating of aminodextran in which each particle comprises a solid metallic core coated either with biodegradable, crosslinked or condensed layers of type B, alkali cured gelatin of Bloom 60 to 225 and an aminodextran, said process comprising;

(a) (i) (1) preparing metallic core particles in said gelatin or (2) adsorbing as a ...

LEVEL 1 - 29 OF 225 PATENTS

5,465,103

<=2> GET 1st DRAWING SHEET OF 6

Nov. 7, 1995

Display device with coordinate input function

INVENTOR: Yoshioka, Kazuo, Nagasaki, Japan

... [\*1] for both displaying images and inputting coordinates, comprising:  
a sensor means for sensing coordinate input detection signals from a control means;

a liquid crystal display panel of two-layer type including an optical phase compensation cell, as a first layer of the liquid crystal display panel and a liquid crystal display cell as a second layer of the liquid crystal display ...

LEVEL 1 - 30 OF 225 PATENTS

5,441,516

<=2> GET 1st DRAWING SHEET OF 5

Aug. 15, 1995

Temporary stent

INVENTOR: Wang, Lixiao, Maple Grove, Minnesota  
Willard, Martin R., Maple Grove, Minnesota  
Tran, Thomas T., Coon Rapids, Minnesota  
Hastings, Roger, Maple Grove, Minnesota

Schmaltz, Dale F., Boulder, Colorado  
Holman, Thomas J., Minneapolis, Minnesota

... [\*15] closely wound helices each comprises at least two oppositely wound windings forming multiple layers.

[\*16] 16. The apparatus of claim 1 wherein the closely wound helices are each of at least the two filar double layer type.

[\*17] 17. The apparatus of claim 16 wherein the closely wound helices are of at least the four filar double layer type.

[\*18] 18. The apparatus of claim 1 wherein a proximal elongate portion of the outer tubular member is comprised of a polymeric/braided composite joined to a distal wire wound portion.

[\*19] 19. The apparatus of claim 18 wherein the polymeric portion of the composite is polyimide.

[\*20] 20. The apparatus of claim 18 wherein the wire wound portion is of at least the four filar double layer type.

[\*21] 21. The apparatus of claim 1 wherein a proximal elongate portion of the inner tubular member is comprised of a polymeric/braided composite joined to a distal wire wound portion.

[\*22] 22. The apparatus of claim 21 wherein the polymeric portion of the composite is polyimide.

[\*23] 23. The apparatus of claim 21 wherein the wire wound portion is of at least the four filar double layer type.

[\*24] 24. The apparatus of claim 1 including means connected to the proximal end portion of the catheter for introducing infusion fluid through one of the tubular members.

[\*25] 25. The apparatus of claim 24 wherein the infusion fluid ...  
PAGE 36

LEVEL 1 - 31 OF 225 PATENTS

5,432,038

<=2> GET 1st DRAWING SHEET OF 1

Jul. 11, 1995

Process for producing an organic photosensitive material  
preventing blushing

INVENTOR: Katsukawa, Masato, Osaka, Japan  
Tanaka, Masashi, Osaka, Japan

... [\*2] process for production according to claim 1, wherein the coefficient k is a number which is 0.13 or smaller.

[\*3] 3. A process for production according to claim 1, wherein said electrophotographic photosensitive material is of the single layer type containing a charge-generating material, a charge-transporting material and a binder resin.

[\*4] 4. A process for production according to claim 1, wherein said weight percentage (C) is from 0.1 to ...  
LEVEL 1 - 32 OF 225 PATENTS

5,428,244

<=2> GET 1st DRAWING SHEET OF 12

Jun. 27, 1995

Semiconductor device having a silicon rich dielectric layer

INVENTOR: Segawa, Mizuki, Kyoto, Japan  
Kato, Yoshiaki, Hyogo, Japan  
Nakaoka, Hiroaki, Osaka, Japan

... [\*3] A semiconductor device as in either claim 1 or claim 2, further comprising a dielectric layer for passivation, said passivation dielectric layer being formed on said dielectric layer type, being composed of a chemical compound which is the same compound that said dielectric layer is composed of, and having a silicon content closer to a silicon content according to the stoichiometric composition formula, compared to the dielectric layer.

[\*4] ...

LEVEL 1 - 33 OF 225 PATENTS

5,420,052

<=2> GET 1st DRAWING SHEET OF 2

May 30, 1995

Method of fabricating a semiplanar heterojunction bipolar transistor

INVENTOR: Morris, Francis J., Plano, Texas  
Yang, Jau-Yuann, Richardson, Texas  
Plumton, Donald L., Dallas, Texas  
Yuan, Han-Tzong, Dallas, Texas

... [\*1] layer;

forming a collector plug region through a selected portion of the collector layer to the subcollector layer;

forming a base layer on the collector layer and the collector plug region;  
forming an emitter layer type on the base layer;  
forming an emitter cap layer on the emitter layer;  
forming a collector contact on the collector plug region;  
forming an emitter contact on the emitter cap layer;  
forming a base contact on the ...

PAGE 39

LEVEL 1 - 34 OF 225 PATENTS

5,401,549

Mar. 28, 1995

Optical information recording medium

INVENTOR: Watase, Kenta, Tokyo, Japan

... [\*1] layer is overlaid on both said reflective layer in said ROM region portion and a recording portion of the substrate in said recording region, said recording layer being of a multi-layer type comprising a dielectric layer and a magnetic layer.

[\*2] 2. The optical information recording medium as claimed in claim 1, further comprising an additional reflective layer which is overlaid on said recording ...

PAGE 40

LEVEL 1 - 35 OF 225 PATENTS

5,390,208

<=2> GET 1st DRAWING SHEET OF 3

Feb. 14, 1995

Strained quantum well type semiconductor laser device

INVENTOR: Kasukawa, Akihiko, Tokyo, Japan  
Kikuta, Toshio, Tokyo, Japan

What is claimed is:

[\*1] 1. A strained quantum well layer type semiconductor laser device comprising a light emitting active layer of a multilayer structure including a quantum well layer and a barrier layer and a pair of light confining layers ...

... [\*1]  $y P 1 - y$  ( $0 < y \leq 1$ ) and the barrier layer and/or the light confining layers are made of  $In 1 - x Ga x P$  ( $0 < x \leq 1$ ).

[\*2] 2. A strained quantum well layer type semiconductor laser device according to claim 1, wherein the InAs y P 1 - y strained quantum well layer satisfies inequality:

SYMBOL OMITTED epsilon w x L w SYMBOL OMITTED < 45(% x nm),

where w is the ratio of deformation (%) and Lw is the thickness (nm) of each component layer of the strained quantum well layer.

[\*3] 3. A strained quantum well layer type semiconductor laser device according to claim 1, wherein the In 1 - x Ga x P barrier layer and each of the In 1 - x Ga x P light confining layers satisfy ...

... [\*3] OMITTED < 45(% x nm),

where s is the ratio of deformation (%) and Ls is the thickness (nm) of each component layer of the barrier layer and the light confining layers.

[\*4] 4. A strained quantum well layer type semiconductor laser device according to claim 1, wherein InAs y P 1 - y (0 < y <= 1) has a value for compositional ratio y between 0.3 and 0.6.

LEVEL 1 - 36 OF 225 PATENTS

5,387,564

Feb. 7, 1995

Molding and calcining of zeolite powder

INVENTOR: Takeuchi, Tatsuro, Tsukuba, Japan  
Mouri, Motoya, Tsuchiura, Japan  
Okabayashi, Saji, Kitakanbara, Japan  
Miyamura, Shoichi, Kitakanbara, Japan

... [\*21] a) a zeolite;

(b) a beta 1,3-glucan in an amount of 0.1-20 parts by weight in relation to 100 parts by weight of the zeolite; and

(c) a 1:1 layer-type clay mineral and a 2:1 layer clay mineral in a total amount of 5-50 parts by weight in relation to 100 parts by weight of the zeolite; and

(ii) at least ...

LEVEL 1 - 37 OF 225 PATENTS

5,374,328

<=2> GET 1st DRAWING SHEET OF 9

Dec. 20, 1994

Method of fabricating group III-V compound

INVENTOR: Remba, Ronald D., Sunnyvale, California  
Brunemeier, Paul E., Sunnyvale, California  
Schmukler, Bruce C., Mountain View, California  
Strifler, Walter A., Sunnyvale, California  
Rosenblatt, Daniel H., Belmont, California

... [\*5] 1-x As wherein  $(0 \leq y \leq 0.2)$  and  $(0.2 < x \leq 1.0)$ .

[\*6] 6. A method of making a semiconductor device comprising the steps of:  
fabricating a structure by

(i) growing one or more layers of the type X a Y 1-a As, where X is an atom selected from the group of IIIA atoms and Y is a different atom selected from the group of IIIA atoms, and where  $(0 < a \leq 1)$  upon a semiconductor ...

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LEVEL 1 - 38 OF 225 PATENTS

5,324,980

<=2> GET 1st DRAWING SHEET OF 24

Jun. 28, 1994

Multi-layer type semiconductor device with semiconductor element layers stacked in opposite direction and manufacturing method thereof

INVENTOR: Kusunoki, Shigeru, Hyogo, Japan

What is claimed is:

[\*1] 1. A multi-layer type semiconductor device, comprising:  
a substrate having a main surface;

a first semiconductor element layer formed on said main surface of said substrate and including a first semiconductor element having an active ...

... [\*3] insulating layer.

[\*4] 4. The device of claim 3, including a conductor filling said through-hole and contacting opposite surfaces of said first and second semiconductor element layers.

[\*5] 5. A multi-layer type semiconductor device, comprising:  
a substrate having a main surface;



a first semiconductor element layer formed on said main surface of said substrate and including a first semiconductor element having an active ...

... [\*5] contact with said insulating layer and being oriented back-to-back on said first and second semiconductor element layers, each of said regions including one or more of the semiconductor elements.

[\*6] 6. A multi-layer type semiconductor device, comprising:  
a substrate having a main surface;

a first semiconductor element layer formed on said main surface of said substrate and including a first semiconductor element having an active ...

... [\*6] second semiconductor element layers.

[\*7] 7. The device of claim 6, wherein a through-hole is formed only through said field oxide layer and said interlayer insulation film.

[\*8] 8. A multi-layer type semiconductor device, comprising:  
a substrate having a main surface;

Pat. No. 5324980, \*8

a first semiconductor element layer formed on said main surface of said substrate and including a first semiconductor element having an active ...

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LEVEL 1 - 39 OF 225 PATENTS

5,324,678

<=2> GET 1st DRAWING SHEET OF 24

Jun. 28, 1994

Method of forming a multi-layer type semiconductor device  
with semiconductor element layers stacked in opposite  
directions

INVENTOR: Kusunoki, Shigeru, Hyogo, Japan

What is claimed is:

[\*1] 1. A method of manufacturing a multi-layer type semiconductor device comprising the steps of;

forming a base member by successively stacking, on a main surface of a first substrate, a first semiconductor layer, an insulating layer and a second ...

... [\*1] semiconductor device by using said first semiconductor layer as a base with an exposed surface of said first semiconductor layer directed upward.

[\*2] 2. A method of manufacturing a multi-layer type semiconductor device according to claim 1, wherein the step of forming the base member includes the steps of;

bonding a first member including said first semiconductor layer formed on said first substrate, with a ...

... [\*2] said insulating layer and said first semiconductor layer are opposed to each other, and

thinning said third substrate the expose said second semiconductor layer.

[\*3] 3. A method of manufacturing a multi-layer type semiconductor device comprising the steps of;

forming perforations through a first substrate;

filling said perforations with conductors,

successively forming a first semiconductor layer on a main surface of a second ...

LEVEL 1 - 40 OF 225 PATENTS

5,291,248

<=2> GET 1st DRAWING SHEET OF 8

Mar. 1, 1994

LED carriage selectively movable in two directions

INVENTOR: Isobe, Minoru, Tokyo, Japan

... [\*3] L-shaped first block, an L-shaped second leaf spring having one end fixed to one end of the first block, and the other end fixed to a right end of the frame, a stacked-layer type of second piezoelectric element adapted to deform itself in response to an application of a voltage by a power source for deforming the second leaf spring, the second piezoelectric element being fixed to the ...

... [\*5] comprises an L-shaped first block, an L-shaped leaf spring having one end fixed to one end of the first block, and the other end fixed to one end of a frame, a stacked-layer type of second piezoelectric element adapted to deform itself in response to an application of a voltage by a power source for deforming the leaf spring, the second piezoelectric element being fixed to the other ...

... [\*18] L-shaped first block, an L-shaped second leaf spring having one end fixed to one end of the first block, and the other end fixed to a right end of the frame, a stacked-layer type of second piezoelectric element adapted to deform itself in response to an application of a voltage by a power source for

deforming the second leaf spring, the second piezoelectric element being fixed to the ...

... [\*20] comprises an L-shaped first block, an L-shaped leaf spring having one end fixed to one end of the first block, and the other end fixed to one end of a frame, a stacked-layer type of second piezoelectric element adapted to deform itself in response to an application of a voltage by a power source for deforming the leaf spring, the second piezoelectric element being fixed to the other ...

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LEVEL 1 - 41 OF 225 PATENTS

5,289,486

<=2> GET 1st DRAWING SHEET OF 5

Feb. 22, 1994

Semiconductor luminous element and superlattice structure

INVENTOR: Iga, Kenichi, Machida, Japan  
Koyama, Fumio, Hino, Japan  
Takagi, Takeshi, Ibaraki, Japan

... [\*8] between the active layer and the multi-quantum barrier layer.

[\*9] 9. A superlattice structure, comprising alternating layers of at least two types of crystals having different energy gaps,

wherein the energy gaps of adjacent crystal layers are such that the type of crystal having the smaller energy gap of the adjacent layers has an energy gap which is smaller than that of a portion of the superlattice structure on a side through which electrons or holes enter the superlattice structure, and

wherein the thicknesses and structures of the adjacent crystal ...

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LEVEL 1 - 42 OF 225 PATENTS

5,275,714

<=2> GET 1st DRAWING SHEET OF 1

Jan. 4, 1994

Method of producing an absorber layer for solar cells with the aid of electrodeposition

INVENTOR: Bonnet, Dieter, Friedrichsdorf, Federal Republic of Germany  
Ehrhardt, Josef, Hochheim/Main, Federal Republic of Germany  
Hewig, Gert, Alzenau, Federal Republic of Germany

... [\*1] electroplating bath and simultaneously incorporating a third alloy component of Group VIA suspended in the electroplating bath in finely dispersed form by dispersion electrolysis, and

producing a ternary semiconductor layer of the type IB-IIIA-VIA by heat treating the deposited material.

[\*2] 2. The method according to claim 1, wherein the volume percentage of each component of the binary alloy is between about 25% and 75%.

[\*3] 3. The method ...  
LEVEL 1 - 43 OF 225 PATENTS

5,272,031

Dec. 21, 1993

Benzidine derivative and photosensitive material using said derivative

INVENTOR: Hanatani, Yasuyuki, Osaka, Japan  
Iwasaki, Hiroaki, Osaka, Japan

... [\*2] material containing a conductive substrate having thereon a photosensitive layer which contains the benzidine derivative (1) according to claim 1.

[\*3] 3. The photosensitive material according to claim 2, wherein the photosensitive layer is a multi-layer type photosensitive layer comprising an electric charge transferring layer and an electric charge generating layer which are laminated mutually.

[\*4] 4. The multi-layer type photosensitive material according to claim 3, wherein the electric charge transferring layer contains 25 to 200 parts by weight of said benzidine derivative (1) for 100 parts by weight of a ...

... [\*5] compounds, and pyrrolopyrrole compounds.

[\*6] 6. The photosensitive material according to claim 5, wherein the electric charge generating material is an azo compound.

[\*7] 7. The photosensitive material according to claim 2, wherein the photosensitive layer is a single-layer type photosensitive layer comprised of an electric charge transferring material, an electric charge generating material and a binding resin.

[\*8] 8. The photosensitive material according to claim 7, wherein the single-layer type photosensitive layer contains 40 to 200 parts by weight of said benzidine derivative (1) for 100 parts by weight of a binding resin.

[\*9] 9. The photosensitive material according to claim 8, wherein the single-layer type photosensitive layer contains, for 100 parts by weight of a

binding resin, 5 to 500 parts by weight of one or more kinds of an electric charge generating material selected from selenium, ...  
LEVEL 1 - 44 OF 225 PATENTS

5,260,723

<=2> GET 1st DRAWING SHEET OF 10

Nov. 9, 1993

Liquid jet recording head

INVENTOR: Naruse, Osamu, Kanagawa, Japan  
AmeYama, Minoru, Kanagawa, Japan  
Matsumoto, Syuzo, Kanagawa, Japan  
Komai, Hiromichi, Kanagawa, Japan  
Hirata, Tositaka, Tokyo, Japan

... [\*1] between  $0.01 \text{ Kg/mm}^2 >$  and  $300 \text{ Kg/mm}^2 <$  .

[\*2] 2. A liquid jet recording head as claimed in claim 1 wherein said piezo-electric member is a layer-type piezo-electric member.

[\*3] 3. A liquid jet recording head as claimed in claim 1 further comprising a driver unit driving said piezo-electric elements.

[\*4] 4. ...

... [\*6] flow paths.

[\*7] 7. A liquid jet recording head as claimed in claim 6 wherein each of said first piezo-electric member and said second piezo-electric member is a layer-type piezo-electric member.

[\*8] 8. A liquid jet recording head as claimed in claim 6 wherein said elasticity member has a modulus of elasticity between  $0.01 \text{ Kg/mm}^2 >$  and ...

... [\*13] elements in a direction perpendicular to said second flow paths.

[\*14] 14. A liquid jet recording head as claimed in claim 13 wherein said piezo-electric member is a layer-type piezo-electric member.

[\*15] 15. A liquid jet recording head as claimed in claim 13 wherein said elasticity member has a modulus of elasticity between  $0.01 \text{ Kg/mm}^2 >$  and ...

... [\*18] elements in the perpendicular direction to each of said plurality of flow paths.

[\*19] 19. A liquid jet recording head as claimed in claim 18 wherein said piezo-electric member is a layer-type piezo-electric member.

[\*20] 20. A liquid jet recording head as claimed in claim 18 wherein said piezo-electric member has a plurality of grooves which are formed on said piezo-electric ...

PAGE 51

LEVEL 1 - 45 OF 225 PATENTS

5,258,251

Nov. 2, 1993

Hydrazone compound and photosensitive material using said compound

INVENTOR: Hanatani, Yasuyuki, Sakai, Japan  
Iwasaki, Hiroaki, Hirakata, Japan

... [\*1] same or different from one another, and each is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group.

[\*2] 2. The photosensitive material according to claim 1, wherein the photosensitive layer is a multi-layer type photosensitive layer including an electric charge transferring layer which includes the hydrazone compound as the electric charge transferring material, and an electric charge generating layer, which layers are laminated mutually.

[\*3] 3. The photosensitive material according to claim 2, wherein the electric charge transferring layer of the multi-layer type photosensitive layer further includes a binding resin, and the electric charge transferring layer contains 25 to 200 parts by weight of said hydrazone compound for 100 parts by weight of the ...

... [\*4] compounds, and pyrrolopyrrole compounds.

[\*5] 5. The photosensitive material according to claim 4, wherein the electric charge generating material is an azo compound.

[\*6] 6. The photosensitive material according to claim 1, wherein the photosensitive layer is a single-layer type photosensitive layer comprised of an electric charge transferring material, an electric charge generating material and a binding resin.

[\*7] 7. The photosensitive material according to claim 6, wherein the single-layer type photosensitive layer contains 40 to 200 parts by weight of said hydrazone compound for 100 parts by weight of the binding resin.

[\*8] 8. The photosensitive material according to claim 7, wherein the single-layer type photosensitive layer contains, for 100 parts by weight of the binding resin, 2 to 20 parts by weight of one or more kinds of an electric charge generating material selected from selenium, selenium- ...

E 52

LEVEL 1 - 46 OF 225 PATENTS

5,256,508

PAG

Oct. 26, 1993

Hydrazone compound and photosensitive material using said compound

INVENTOR: Hanatani, Yasuyuki, Sakai, Japan  
Iwasaki, Hiroaki, Hirakata, Japan

... [\*1] halogen atom, an alkyl group, an alkoxy group or the following group: [See Original Patent for Chemical Structure Diagram]

[\*2] 2. The photosensitive material according to claim 1, wherein the photosensitive layer is a multi-layer type photosensitive layer including an electric charge transferring layer which includes the hydrazone compound as the electric charge transferring material, and an electric charge generating layer, which layers are laminated mutually.

[\*3] 3. The photosensitive material according to claim 2, wherein the electric charge transferring layer of the multi-layer type photosensitive layer further includes a binding resin, and the electric charge transferring layer contains 25 to 200 parts by weight of said hydrazone compound for 100 parts by weight of the ...

... [\*4] compounds, and pyrrolopyrrole compounds.

[\*5] 5. The photosensitive material according to claim 4, wherein the electric charge generating material is an azo compound.

[\*6] 6. The photosensitive material according to claim 1, wherein the photosensitive layer is a single-layer type photosensitive layer comprised of an electric charge transferring material, an electric charge generating material and a binding resin.

[\*7] 7. The photosensitive material according to claim 6, wherein the single-layer type photosensitive layer contains 40 to 200 parts by weight of said hydrazone compound for 100 parts by weight of the binding resin.

[\*8] 8. The photosensitive material according to claim 7, wherein the single-layer type photosensitive layer contains, for 100 parts by weight of the binding resin, 2 to 20 parts by weight of one or more kinds of an electric charge generating material selected from selenium, selenium- ...

E 53

PAG

LEVEL 1 - 47 OF 225 PATENTS

5,254,423

<=2> GET 1st DRAWING SHEET OF 1

Oct. 19, 1993

Electrophotographic photosensitive member, and  
electrophotographic apparatus, device unit and facsimile  
machine having the photosensitive member

INVENTOR: Mayama, Shinya, Yamato, Japan  
Fujimura, Naoto, Yokohama, Japan  
Yoshihara, Toshiyuki, Inagi, Japan  
Sakai, Kiyoshi, Hachioji, Japan  
Anayama, Hideki, Yokohama, Japan  
Ainoya, Hideyuki, Tokyo, Japan  
Aoki, Katsumi, Yokohama, Japan

- ... [\*21] 21. The electrophotographic photosensitive member according to claim 19, wherein said charge generation layer is the surface layer.
- [\*22] 22. The electrophotographic photosensitive member according to claim 18, wherein said photosensitive layer is of a single layer type.
- [\*23] 23. The electrophotographic photosensitive member according to claim 1, wherein said surface layer is a surface protective layer.
- [\*24] 24. The electrophotographic photosensitive member according to claim 1, wherein said electrophotographic photosensitive member has ...

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PA

LEVEL 1 - 48 OF 225 PATENTS

5,247,445

<=2> GET 1st DRAWING SHEET OF 5

Sep. 21, 1993

Control unit of an internal combustion engine control unit  
utilizing a neural network to reduce deviations between  
exhaust gas constituents and predetermined values

INVENTOR: Miyano, Hideyo, Niza, Japan  
Suzaki, Yukihiro, Nerima, Japan  
Takahashi, Fumitaka, Hoya, Japan  
Ogasawara, Ken-ichi, Fujimi, Japan

... [\*7] units as the number of cylinders, and an intermediate layer arranged between said input layer and said output layer; and wherein the units are coupled with predetermined coupling weights only across the layers to form a three-layer type perceptron neural network.

[\*8] 8. A control unit for an internal combustion engine according to claim 7 wherein said control means corrects said coupling weights among the units by applying a back propagation learning method to said three-layer type perceptron neural network, and corrects the correction coefficient for said calculation means.



[\*9] 9. A control unit for an internal combustion engine according to claim 7 wherein said control means corrects ...

... [\*22] units as the number of cylinders, and an intermediate layer arranged between said input layer and said output layer; and wherein the units are coupled with predetermined coupling weights only across the layers to form a three-layer type perceptron neural network.

[\*23] 23. A control unit for an internal combustion engine according to claim 22 wherein said control means corrects said coupling weights among the units by applying a back propagation learning method to said three-layer type perceptron neural network, and corrects the correction coefficient for said calculation means.

[\*24] 24. A control unit for an internal combustion engine according to claim 22 wherein said control means corrects ...  
LEVEL 1 - 49 OF 225 PATENTS

5,244,561

PAGE 55

<=2> GET 1st DRAWING SHEET OF 3

Sep. 14, 1993

Process and apparatus for the electrochemical determination  
of PCO2 in blood

INVENTOR: Calzi, Claudio, Milan, Italy  
Tancredi, Gabrio, Milan, Italy

... [\*3] 3. The process of claim 1, wherein the measurement liquid is high-purity water.

[\*4] 4. The process of claim 1, wherein the measuring cell is a conductivity cell.

[\*5] 5. The process of claim 4, wherein the conductivity cell is of the thin layer type.

[\*6] 6. The process of claim 1, wherein the means of removing ionic impurities are ion exchangers.

[\*7] 7. The process of 6, wherein the ion exchangers are in mixed bed form.

[\*8] 8. The process of claim 7, wherein the ion exchangers ...

... [\*12] 12. The apparatus of claim 10, wherein the measurement liquid is high-purity water.

[\*13] 13. The apparatus of claim 10, wherein the measuring cell is a conductivity cell.

[\*14] 14. The apparatus of claim 13, wherein the conductivity cell is of the thin layer type.

[\*15] 15. The apparatus as claimed in claim 10, wherein the means for removing ionic impurities are ion exchangers.

[\*16] 16. The apparatus of claim 10, wherein the ion exchangers are in mixed bed form.

[\*17] 17. The ...

LEVEL 1 - 50 OF 225 PATENTS

5,242,839

<=2> GET 1st DRAWING SHEET OF 6

Sep. 7, 1993

Method of manufacturing an integrated photoelectric receiving device

INVENTOR: Oh, Kwang-Ryong, Daejeon, Republic of Korea  
Lee, Yong-Tak, Daejeon, Republic of Korea

... [\*1] layer, an etching stopper layer and an absorption layer on the substrate etched;

c) removing the absorption layer excluding the photodetector forming area on the substrate by the selective etchant;

d) sequentially removing the etching stopper layer and the type n-channel layer between the photodetector and the transistor forming areas to electrically insulate the photodetector and the transistor;

e) sequentially forming a p-type InP layer and a p-type InGaAs layer on the ...  
PAGE 57

LEVEL 1 - 51 OF 225 PATENTS

5,240,964

<=2> GET 1st DRAWING SHEET OF 1

Aug. 31, 1993

Process for producing urethane foam with high density skin

INVENTOR: Ohmura, Hirokazu, Niiza, Japan  
Yoshimura, Kimio, Urawa, Japan  
Narumi, Satoshi, Tochigi, Japan

What is claimed is:

[\*1] 1. A process for producing a urethane foam having a high density outer surface layer, of the type wherein a plastic liquid containing di or polyisocyanates, polyols, a catalyst, low-molecular polyols used as a crosslinker or a chain extender, a blowing agent consisting of water, and an assistant is ...

PAGE 58

LEVEL 1 - 52 OF 225 PATENTS

5,236,755

<=2> GET 1st DRAWING SHEET OF 1

Aug. 17, 1993

Optical recording elements

INVENTOR: Howe, Steven D., Suffolk, England  
Dorey, Lynn Y., Essex, England

... [\*5] element as claimed in claims 1, 2, 3, or 4 in which the element is in the form of a tape.

[\*6] 6. An element as claimed in any one of claims 1 to 4, wherein the absorbing layer is of the type which is thermally deformed to form optically readable pits when subject to heating by laser radiation of said given wavelength.

[\*7] 7. An optical recording element as claimed in any one of claims 1 to 4, ...

PAGE 59

LEVEL 1 - 53 OF 225 PATENTS

5,214,664

<=2> GET 1st DRAWING SHEET OF 15

May 25, 1993

Multiple wavelength semiconductor laser

INVENTOR: Paoli, Thomas L., Los Altos, California

... [\*4] emitting multiple wavelength solid state laser, comprising:  
a plurality of contiguous layers of semiconductor material deposited on a substrate, one of said layers comprising a multiple quantum well active layer of the type wherein at least two quantum wells contained therein are formed such that one quantum level of a first quantum well is at the same energy level as a different quantum level of the second quantum well;

resonant ...

... [\*18] multiple wavelength solid state laser, comprising:

a substrate;  
a first cladding layer disposed on said substrate;  
a multiple quantum well active layer disposed on said first cladding layer of the type having at least two adjacent quantum wells, a first of said quantum wells having a first energy bandgap between the lowest energy level of its conduction band and the uppermost level of its valence band and a ...  
... [\*23] multiple wavelength solid state laser, comprising:  
a substrate;  
a first cladding layer disposed on said substrate;  
a multiple quantum well active layer disposed on said first cladding layer of the type having at least two adjacent quantum wells, a first of said quantum wells having a first thickness and a second of said quantum wells having a second thickness which is greater than said first thickness, ...

E 60

LEVEL 1 - 54 OF 225 PATENTS

5,213,926

May 25, 1993

Phenylenediamine derivative and photosensitive material  
using said derivative

INVENTOR: Hanatani, Yasuyuki, Sakai, Japan  
Iwasaki, Hiroaki, Hirakata, Japan

... [\*2] material containing a conductive substrate having thereon a photosensitive layer which contains the phenylenediamine derivative (1) according to claim 1.

[\*3] 3. The photosensitive material according to claim 2, wherein the photosensitive layer is a multi-layer type photosensitive layer comprising an electric charge transferring layer on an electric charge generating layer which are laminated mutually.

[\*4] 4. The multi-layer type photosensitive material according to claim 3, wherein the electric charge transferring layer contains 25 to 200 parts by weight of said phenylenediamine derivative (1) for 100 parts by weight of a ...

... [\*5] compounds, and pyrrolopyrrole compounds.

[\*6] 6. The photosensitive material according to claim 5, wherein the electric charge generating material is an azo compound.

[\*7] 7. The photosensitive material according to claim 2, wherein the photosensitive layer is a single-layer type photosensitive layer comprised of an

electric charge transferring material, an electric charge generating material and a binding resin.

[\*8] 8. The photosensitive material according to claim 7, wherein the single-layer type photosensitive layer contains 40 to 200 parts by weight of said phenylenediamine derivative (1) for 100 parts by weight of a binding resin.

[\*9] 9. The photosensitive material according to claim 8, wherein the single-layer type photosensitive layer contains, for 100 parts by weight of a binding resin, 2 to 20 parts by weight of one or more kinds of an electric charge generating material selected from the group ...

LEVEL 1 - 55 OF 225 PATENTS

5,200,969

<=> GET 1st DRAWING SHEET OF 15

Apr. 6, 1993

Switchable multiple wavelength semiconductor laser

INVENTOR: Paoli, Thomas L., Los Altos, California

... [\*1] two different output wavelengths, comprising:

a laser body of the type including a plurality of contiguous layers of semiconductor material, located in an optical path, at least first and second portions of said layers of the type providing carrier quantization in at least one dimension, wherein said first and second portions are formed such that one quantum level of said first portion is at the same energy level as a different quantum ...

... [\*2] different output wavelengths, comprising:

a laser body of the type including a plurality of contiguous layers of semiconductor material, located in an optical path, at least a first and second portions of said layers of the type providing carrier quantization in at least one dimension, wherein said first and second portions thereof are formed such that one quantum level of said first portion is at the same energy level as a different quantum ...

LEVEL 1 - 56 OF 225 PATENTS

5,196,143

Mar. 23, 1993

Mixed metal hydroxide-clay adducts as thickeners for water and other hydrophylic fluids

INVENTOR: Burba, III, John L., Angleton, Texas  
Barnes, Audrey L., Lake Jackson, Texas

... [\*13] saconite, sepiolite, vermiculite, attapulgite, and Fuller's earth.

[\*14] 14. The adduct or reaction product of claim 1 wherein the mineral clay is at least one of the classes consisting of amorphous clays of the allophane group and crystalline clays of the 2-layer type, 3-layer type, expanding type, non-expanding type, elongate, regular mixed layer type, and chain structure type.

[\*15] 15. The adduct or reaction product of claim 1 wherein the mineral clay is bentonite.

[\*16] 16. The adduct or reaction product of claim 1 wherein the mineral clay is beneficiated bentonite.

[\*17] 17. The adduct or reaction ...  
LEVEL 1 - 57 OF 225 PATENTS

5,189,567

<=2> GET 1st DRAWING SHEET OF 3

Feb. 23, 1993

High speed switching circuit for controlling current flow in  
a bridge circuit coil for use in a magneto-optic direct  
overwrite system

INVENTOR: Mody, Hemant K., Rochester, New York

What is claimed is:

[\*1] 1. A direct over-write magneto-optic recording apparatus for recording digital information in a magnetic recording layer of the type having vertically oriented magnetic domains, said digital information identified by a digital information source, said apparatus comprising:

(a) means for scan-irradiating the recording layer with a beam of ...

... [\*3] by claim 2, wherein said switching elements are comprises of triacs.

[\*4] 4. A direct over-write magneto-optic recording apparatus for recording digital information in a magnetic recording layer of the type having vertically oriented magnetic domains, wherein an information data source provides control signals identifying data to be stored by said recording apparatus, said apparatus comprising:

(a) means for scan- ...

... [\*6] alternates directions during each cycle of said predetermined frequency.

[\*7] 7. A direct over-write magneto-optic recording apparatus for recording digital information in a magnetic recording layer of the type having magnetic domains with a plurality of vertical orientations, wherein said digital information to be recorded is represented by control signals determining a representation of said digital information by said recording layer, ...

PAGE 64

LEVEL 1 - 58 OF 225 PATENTS

5,189,500

<=2> GET 1st DRAWING SHEET OF 24

Feb. 23, 1993

Multi-layer type semiconductor device with semiconductor element layers stacked in opposite directions and manufacturing method thereof

INVENTOR: Kusunoki, Shigeru, Hyogo, Japan

What is claimed is:

[\*1] 1. A multi-layer type semiconductor device comprising;  
a transparent substrate,

a photosensor layer formed on said transparent substrate and including photosensor elements for detecting light passing through said transparent substrate and converting the ...

... [\*1] photosensor elements of said photosensor layer and electrically connected to said circuit layer via said through holes for displaying results of processing output from said circuit layer.

[\*2] 2. A multi-layer type semiconductor device according to claim 1, further comprising a light shielding layer interposed between said photosensor layer and said circuit layer for preventing light traveling through said photosensor layer toward said circuit layer from entering said circuit layer.

[\*3] 3. A multi-layer type semiconductor device according to claim 1, which is formed of materials penetrable to light as a single chip.

[\*4] 4. A multi-layer type semiconductor device according to claim 3, which, formed as the single chip, has a light transmittance of at least 5%.

[\*5] 5. A multi-layer type semiconductor device according to claim 1, wherein said display element layer includes transmission type liquid crystal display elements for giving a display based on variations of light passing therethrough, ...

... [\*5] layer formed between said display element layer and said circuit layer and including light emitting elements for projecting light to said liquid crystal display elements.

[\*6] 6. A multi-layer type semiconductor device according to claim 5, further comprising a light shielding layer interposed between said light emitting element layer and said circuit layer for preventing light traveling from said light emitting element layer toward said circuit layer from entering said circuit layer.

[\*7] 7. A multi-layer type semiconductor device according to claim 1, wherein said display element layer includes reflection type liquid crystal display elements for giving a display based on variations of reflected light.

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Pat. No. 5189500, \*7

[\*8] 8. A multi-layer type semiconductor device according to claim 1, wherein said display element layer includes light emitting elements for giving a display based on self-emission of light.

[\*9] 9. A multi-layer type semiconductor device according to claim 8, further comprising a light shielding layer interposed between said display element layer and said circuit layer for preventing light traveling from said display element layer toward said circuit layer from entering said circuit layer.

[\*10] 10. A multi-layer type semiconductor device comprising;  
a transparent substrate,

a display element layer including display elements and formed on said transparent substrate such that a display given by said display elements is visible ...

... [\*10] connected to said circuit layer via said through holes for converting an amount of information received from outside into an electric signal for processing by said circuit layer.

[\*11] 11. A multi-layer type semiconductor device according to claim 10, wherein said sensor layer includes a photosensor element for detecting light.

[\*12] 12. A multi-layer type semiconductor device according to claim 10, wherein said sensor layer includes a temperature sensing element for detecting temperature.

[\*13] 13. A multi-layer type semiconductor device according to claim 10, wherein said sensor layer includes a pressure sensing element for detecting pressure.

[\*14] 14. A multi-layer type semiconductor device according to claim 10, wherein said sensor layer includes a sensing element for detecting radiation.



[\*15] 15. A multi-layer type semiconductor device comprising;

a substrate defining perforations and having conductors formed in said perforations,

a first circuit layer formed on said substrate and including an electric circuit electrically connected to said ...

LEVEL 1 - 59 OF 225 PATENTS

5,189,297

<=2> GET 1st DRAWING SHEET OF 2

Feb. 23, 1993

Planar double-layer heterojunction HgCdTe photodiodes and methods for fabricating same

INVENTOR: Ahlgren, William L., Goleta, California

... [\*19] atoms selected for type-converting the underlying collector layer to an opposite type of electrical conductivity;

illuminating the dopant layer and the underlying surface of the collector layer with the source; and

diffusing the dopant layer into the underlying collector layer thereby type-converting the underlying collector layer to an opposite type of conductivity.

[\*20] 20. A method as defined in claim 13 wherein the step of forming a base layer is accomplished by forming an n-type ...

... [\*21] depositing the liberated dopant atoms over the surface of the collector layer, the dopant atoms being deposited upon the surface only where a photodiode is not desired; and

diffusing the deposited dopant atoms into the underlying collector layer thereby type-converting the underlying collector layer to an n-type of conductivity.

[\*22] 22. A method as defined in claim 13 and further comprising a step of depositing a passivation layer at least over the ...

LEVEL 1 - 60 OF 225 PATENTS

5,187,680

<=2> GET 1st DRAWING SHEET OF 15

Feb. 16, 1993

Neural net using capacitive structures connecting input lines and differentially sensed output line pairs

INVENTOR: Engeler, William E., Scotia, New York

... [\*11] lines that are identified by the same ordinal number connected to be receptive of the same input signal, thereby to provide a neural network layer.

[\*12] 12. A plurality, L in number, of neural net layers of the type set forth in claim 11, respectively identified by consecutive ordinal numbers zeroeth through (L - 1)<th>, L being a positive integer, the non-linear amplifiers of the processors ...

... [\*18] lines that are identified by the same ordinal number connected to be receptive of the same input signal, thereby to provide a neural network layer.

[\*19] 19. A plurality, L in number, of neural net layers of the type set forth in claim 18, respectively identified by consecutive ordinal numbers zeroeth through (L - 1)<th>, L being a positive integer, the non-linear amplifiers of the processors ...

... [\*27] lines that are identified by the same ordinal number connected to be receptive of the same input signal, thereby to provide a neural network layer.

[\*28] 28. A plurality, L in number, of neural net layers of the type set forth in claim 27, respectively identified by consecutive ordinal numbers zeroeth through (L - 1)<th>, L being a positive integer, the non-linear amplifiers of the processors ...

LEVEL 1 - 61 OF 225 PATENTS

5,185,228

Feb. 9, 1993

Electrophotosensitive material containing p-benzylbiphenyl

INVENTOR: Maeda, Tatsuo, Kobe, Japan  
Katsukawa, Masato, Ibaraki, Japan  
Iwasaki, Hiroaki, Hirakata, Japan  
Mizuta, Yasufumi, Kishiwada, Japan

... [\*3] benzylbiphenyl is included in an amount of 20 to 150 parts by weight for 100 parts by weight of m-phenylenediamine.

[\*4] 4. An electrophotosensitive material according to claim 2, wherein the layer is a single-layer type photosensitive layer containing a charge generating material.

[\*5] 5. An electrophotosensitive material according to claim 4, wherein the charge generating material is a perylene compound.

[\*6] 6. An electrophotosensitive material according to claim 2, wherein the

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(InterLock SMTP Gateway 3.0 for dmorris@watson.ibm.com);  
Tue, 22 Dec 1998 12:45:15 -0500  
Message-Id: <199812221745.AA26467@prod.lexis-nexis.com>  
Received: by prod.lexis-nexis.com (Internal Mail Agent-1);  
Tue, 22 Dec 1998 12:45:15 -0500  
Date: Tue, 22 Dec 1998 12:45:13 -0500  
From: lexis-nexis@prod.lexis-nexis.com (LEXIS(R)/NEXIS(R) Print Delivery)  
To: dmorris@watson.ibm.com  
Subject: LEXIS(R)/NEXIS(R) Print Request Job 68990, 2 of 4

...

... [\*7] contained in an amount of 20 to 150 parts by weight for 100 parts by weight of charge transfer material.

[\*8] 8. An electrophotosensitive material according to claim 1, wherein the layer is a single-layer type photosensitive layer containing a charge generating material.

[\*9] 9. An electrophotosensitive material according to claim 8, wherein the charge generating material is a perylene compound.

[\*10] 10. An electrophotosensitive material according to claim 1, wherein  
the ...

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LEVEL 1 - 62 OF 225 PATENTS

5,179,457

<=2> GET 1st DRAWING SHEET OF 7

Jan. 12, 1993

Liquid crystal display device with birefringent film between  
the substrates of the liquid crystal

INVENTOR: Hirataka, Jun-ichi, Hitachi, Japan  
Kondo, Katsumi, Katsuta, Japan  
Tomiooka, Yasushi, Hatoyama, Japan  
Imazeki, Shuji, Hatoyama, Japan  
Taniguchi, Yoshio, Hino, Japan

... [\*9] pair of electrode structures,

a liquid crystal layer sandwiched between said pair of substrates and  
electrode structures, and

an optical birefringent device disposed between said pair of substrates including a solid layer type structure substantially transparent to a light employed wherein a pattern is formed in said structure by two areas, each area having a different birefringent property and said pattern is arranged within the ...

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LEVEL 1 - 63 OF 225 PATENTS

5,169,754

Dec. 8, 1992

Biodegradable particle coatings having a protein covalently immobilized by means of a crosslinking agent and processes for making same

INVENTOR: Siiman, Olavi, Davie, Florida  
Burshteyn, Alexander, Miami Lakes, Florida  
Gupta, Ravinder K., Pembroke Pines, Florida

... [\*1] particles in which each particle comprises a solid core coated with two layers of water soluble gelatin having a plurality of pendant functional groups, said gelatin layers comprising a first layer of type B, alkali cured gelatin of Bloom in the range 60 to 225 and a second layer of type A, acid cured gelatin of Bloom in the range 60 to 300, and said layers on the individual particles being crosslinked by the action of a chemical crosslinking agent such that aid particles can be ...

... [\*27] colloidal sized solid core material;

(b) a gelatin coating adsorbed onto the surface of said solid core and crosslinked thereon by a chemical crosslinking agent, said gelatin coating comprising first layer of type B, alkali cured gelatin of Bloom in the range 60 to 225 and a second layer of type A, acid cured gelatin of Bloom in the range of 60 to 300;

(c) an antibody; and

(d) a bridging group having an end covalently bonded to said crosslinked gelatin surface and another end covalently ...

... [\*43] a) contacting a solution containing a biological substance with an antibody covalently bound to the surface of a crosslinked gelatin coated solid core particle wherein said gelatin coating comprises a first layer of type B, alkali cured gelatin of Bloom in the range 60-225 and a second layer of type A, acid cured gelatin of Bloom in the range of 60-300;

(b) incubating the mixture of step (a) for a time and at a temperature sufficient to insure the formation of a complex between ...

LEVEL 1 - 64 OF 225 PATENTS

PAGE 7

Nov. 10, 1992

Display device with coordinate input function

INVENTOR: Yoshioka, Kazuo, Nagasaki, Japan

... [\*1] for both displaying images and inputting coordinates, comprising:  
a sensor means for sensing coordinate input detection signals from a control means;

a liquid crystal display panel of two-layer type including an optical phase liquid crystal compensation cell as a first layer of the liquid crystal display panel and a liquid crystal display cell as a second layer of the liquid ...

... [\*1] signals to said sensor means.

[\*2] 2. A display device with coordinate input function as set forth in claim 1, wherein an image display screen of the liquid crystal display panel of two-layer type is divided into plural areas to be separately driven.

PAGE 72

LEVEL 1 - 65 OF 225 PATENTS

Sep. 15, 1992

Semiconductor device having thin film wiring layer of aluminum containing carbon

INVENTOR: Kato, Takashi, Sagami, Japan  
Ito, Takashi, Kawasaki, Japan  
Maeda, Mamoru, Tama, Japan

... [\*8] carbon greater than an atomic percent of carbon contained in said third layer.

[\*9] 9. A semiconductor device as claimed in claim 5 in which a plurality of pairs of said third layer type and said fourth layer type are provided on said fourth layer in alternate succession so that each third layer type is sandwiched between two fourth layer types.

[\*10] 10. A semiconductor device as claimed in claim 1, in which grains of said second layer are generally oriented on a (200) plane.

[\*11] 11. A semiconductor device as claimed ...  
LEVEL 1 - 66 OF 225 PATENTS

PAGE 73

5,146,542

<=2> GET 1st DRAWING SHEET OF 12

Sep. 8, 1992

Neural net using capacitive structures connecting output  
lines and differentially driven input line pairs

INVENTOR: Engeler, William E., Scotia, New York

... [\*14] said training period of time for generating an error signal  
identified by the same ordinal number as said processor generating it.

[\*15] 15. A plurality, L in number, of neural net layers of the type set  
forth in claim 14, respectively identified by consecutive ordinal numbers  
zeroeth through (L - 1)<th>, L being a positive integer, the output ports of  
the processors in ...

... [\*26] input lines and the one of said (M + 1)<th> > and 2M<th> > input  
lines identified by ordinal number M higher.

[\*27] 27. A plurality, L in number, of neural net layers of the type set  
forth in claim 25, respectively identified by consecutive ordinal numbers  
zeroeth through (L - 1)<th>, L being a positive integer, the non-linear  
amplifiers of the processors ...

... [\*31] lines that are identified by the same ordinal number connected to  
be receptive of the same input signal, thereby to provide a neural network  
layer.

[\*32] 32. A plurality, L in number, of neural net layers of the type set  
forth in claim 31, respectively identified by consecutive ordinal numbers  
zeroeth through (L - 1)<th>, L being a positive integer, the non-linear  
amplifiers of the processors ...

... [\*33] said training period of time for generating an error signal  
identified by the same ordinal number as said processor generating it.

[\*34] 34. A plurality, L in number, of neural net layers of the type set  
forth in claim 33, respectively identified by consecutive ordinal numbers  
zeroeth through (L - 1)<th>, L being a positive integer, the output ports of  
the processors in ...

LEVEL 1 - 67 OF 225 PATENTS

5,141,684

<=2> GET 1st DRAWING SHEET OF 2

PAGE 74

Aug. 25, 1992

Method of preparing urethane foam articles

INVENTOR: Yoshimura, Kimio, Urawa, Japan  
Narumi, Satoshi, Tokyo, Japan

What is claimed is:

[\*1] 1. A method of preparing a urethane foam article having a high density outer surface layer, of the type wherein a plastic liquid containing isocyanates, polyols, a catalyst, a blowing agent, an assistant and other additives is poured into a mold through a one-shot molding process while maintaining the ...

... [\*4] 1-substituted imidazole compound,  
1,8-diazabicyclo(5,4,0)-7-undecene and an organic acid salt thereof.

[\*5] 5. A method of preparing a urethane foam article having a high density outer surface layer, of the type wherein a plastic liquid containing isocyanates, polyols, a catalyst, a blowing agent, an assistant and other additives is poured into a mold through a one-shot molding process while maintaining the ...

PAGE 75

LEVEL 1 - 68 OF 225 PATENTS

5,132,132

<=2> GET 1st DRAWING SHEET OF 3

Jul. 21, 1992

Coating method for magnetic recording medium

INVENTOR: Watanabe, Masaru, Nishinomiya, Japan  
Hirose, Satoshi, Amagasaki, Japan

... [\*1] as to form a lower layer on said support continuously travelling and then coating on said lower layer a second magnetic coating solution so as to form an upper layer thereon to thereby produce a two-layer type magnetic recording medium, said method comprising the steps of coating said first magnetic coating solution on said support by a first die including first and second lip portions which are in ...

PAGE 76

LEVEL 1 - 69 OF 225 PATENTS

5,128,229

<=2> GET 1st DRAWING SHEET OF 2

Jul. 7, 1992

Electrophotosensitive material and method of manufacturing  
the same



INVENTOR: Katsukawa, Masato, Ibaraki, Japan  
Kimoto, Keizo, Hirakata, Japan  
Tsujita, Mitsuji, Osaka, Japan  
Miura, Satoru, Shijonawate, Japan

We claim:

[\*1] 1. An electrophotosensitive material having a single-layer type photosensitive layer formed on the surface of a conductive substrate, wherein the photosensitive layer includes a charge generating material a polycarbonate resin as a binding resin, said polycarbonate resin being ...

... [\*2] according to claim 1, wherein the photosensitive layer includes a perylene compound as the charge generating material..

[\*3] 3. A method of manufacturing an electrophotosensitive material, said electrophotosensitive material being a single-layer type photosensitive layer formed on the surface of a conductive substrate, wherein the photosensitive layer a charge generating material includes a polycarbonate resin as a binding resin, said polycarbonate resin being ...

... [\*5] compound represented by formula (II) is included in an amount of 40 to 200 parts by weight per 100 parts by weight of the polycarbonate resin.

[\*6] 6. An electrophotosensitive material having a single-layer type photosensitive layer formed on the surface of a conductive substrate, wherein the photosensitive layer includes a charge generating material a polycarbonate resin represented by the following formula (I): [See Original Patent ...

... [\*6] said photosensitive layer being not greater than  $2.5 \times 10^{-3}$  >  $\mu$  1/mg.

[\*7] 7. A method of manufacturing an electrophotosensitive material, said electrophotosensitive material being a single-layer type photosensitive layer formed on the surface of a conductive substrate, wherein the photosensitive layer a charge generating material includes a polycarbonate resin represented by the following formula (I): [See Original Patent ...  
LEVEL 1 - 70 OF 225 PATENTS

5,126,210

<=2> GET 1st DRAWING SHEET OF 2

Jun. 30, 1992

Anodic phosphonic/phosphinic acid duplex coating on valve  
metal surface

INVENTOR: Wieserman, Larry F., Apollo, Pennsylvania  
Wefers, Karl, Apollo, Pennsylvania

Gary A., Natrona, Pennsylvania  
ward S., New Kensington, Pennsylvania

] copper, manganese, molybdenum, chromium, nickel, zinc, vanadium,  
boron, lithium and zirconium; and

duplex layer comprised of:

intermediate layer consisting essentially of a non-porous barrier  
valve metal oxide attached to said base layer; and

acid resistant, functionalized layer of a monomeric  
-containing compound chemically bonded to a surface of said oxide  
functionalized ...

] 9. A layered material comprised of:

base layer of aluminum alloy; and

duplex layer comprised of:

intermediate layer consisting essentially of a non-porous barrier  
aluminum oxide attached to said base layer; and

acid resistant, functionalized layer of an organic monomeric  
-containing compound chemically bonded to a surface of said oxide

10. The layered ...

] A layered material comprised of:

base layer of aluminum or aluminum alloy; and

duplex layer comprised of:

intermediate layer consisting essentially of a non-porous barrier  
aluminum oxide attached to said base layer having a density of 2.8 to  
; being greater than 95 wt. % aluminum oxide, having a thickness in  
of 100 to 5000 Angstrom and ...

LEVEL 1 - 71 OF 225 PATENTS

5,116,692

<=2> GET 1st DRAWING SHEET OF 2

May 26, 1992

Multi-layer type sliding bearing of aluminum alloy and  
method of producing the same

Nitowski,  
Martin, E

... [\*  
titanium,

(b) a

(i) an  
layer typ

(ii) a  
phosphoru  
layer, th

... [\*

(a) a

(b) a

(i) an  
layer typ

(ii) a  
phosphoru  
layer.

[\*10]

... [\*

(a) a

(b) a

(i) an  
layer typ  
3.2 gms/c  
the range

INVENTOR: Mori, Sanae, Nagoya, Japan  
Sakamoto, Masaaki, Nagoya, Japan  
Ishikawa, Hideo, Komaki, Japan  
Nagai, Yoji, Nagoya, Japan

What is claimed is:

[\*1] 1. In a multi-layer type sliding bearing of aluminum alloy, having a backing layer of steel, a bearing layer of aluminum alloy bonded to the backing layer, and an overlay layer, the improvement further comprising a mixture layer of a ...

... [\*1] layer and one element selected from the group consisting of Ni, Co and Fe, said overlay consisting by weight of 0 to 15% Cu, 0 to 20% Sb, and the balance Sn and incidental impurities.

[\*2] 2. A multi-layer type sliding bearing of aluminum alloy, having a backing layer of steel provided on one side thereof with a rear face-plating layer provided on rear face thereof, a bearing layer of aluminum alloy bonded to ...

... [\*2] overlay and one element selected from the group consisting of Ni, Co and Fe, said overlay consisting by weight of 0 to 15% Cu, 0 to 20% Sb, and the balance Sn and incidental impurities.

[\*3] 3. A multi-layer type sliding bearing of aluminum alloy as claimed in claim 2, wherein the rear face-plating layer consists of the same constituents as the overlay, the thickness of the rear face-plating layer being in a range of 0.1 to 5 microns.

[\*4] 4. In a method of producing a multi-layer type sliding bearing of aluminum alloy, comprising the steps of: providing a half cylindrical or cylindrical bearing member made of an aluminum alloy, said bearing member being bonded onto a backing layer of steel; and ...

... [\*4] said mixture layer being constituted by a mixture of the constituents of said overlay and one element selected from the group consisting of Ni, Co and Fe.

[\*5] 5. A method of producing a multi-layer type sliding bearing of aluminum alloy claimed in claim 4, wherein said step of electrolytically providing said overlay layer on said inner face of said bearing member further includes the step of electrolytically ...

LEVEL 1 - 72 OF 225 PATENTS

5,103,329

<=2> GET 1st DRAWING SHEET OF 8

Apr. 7, 1992

Surface stabilized ferroelectric liquid crystal switching  
using proximity effects

INVENTOR: Clark, Noel A., Boulder, Colorado  
Handschy, Mark, Boulder, Colorado

... [\*14] third electrode means, said first and second domain wall forming  
a data value.

[\*15] 15. The apparatus as recited in claim 1, wherein said liquid crystal  
film is a tilted layer type.

[\*16] 16. An apparatus as in claim 1, wherein said electrode gap is spanned  
by a resistive layer.

LEVEL 1 - 73 OF 225 PATENTS

5,087,544

Feb. 11, 1992

Perylene electrophotosensitive material with  
m-phenylenediamine

INVENTOR: Muto, Nariaki, Daito, Japan  
Kakui, Mikio, Mino, Japan  
Sumida, Keisuke, Hirakata, Japan  
Nakazawa, Toru, Osaka, Japan  
Matsumoto, Kazuo, Hirakata, Japan

What is claimed is:

[\*1] 1. An electrophotosensitive material comprising a conductive substrate  
and a single layer type photosensitive layer provided on said conductive  
substrate, said photosensitive layer containing a m-phenylenediamine compound as  
charge-transferring material and a perylene compound as charge-generating  
material, ...

LEVEL 1 - 74 OF 225 PATENTS

5,081,513

<=2> GET 1st DRAWING SHEET OF 5

Jan. 14, 1992

Electronic device with recovery layer proximate to active  
layer

INVENTOR: Jackson, Warren B., San Francisco, California  
Hack, Michael, Mountain View, California

... [\*9] dopant concentration of each of said dopant types in said recovery  
layer is capable of providing substantially the same number of carriers of said

opposite sign to said channel carriers as does a doped layer of that type having a concentration in the range of  $1.5 \times 10^{18}$  to  $4.5 \times 10^{18}$  atoms per  $\text{cm}^3$  .

[\*10] 10. An electronic device including a substantially intrinsic non-single ...

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LEVEL 1 - 75 OF 225 PATENTS

5,059,502

<=2> GET 1st DRAWING SHEET OF 3

Oct. 22, 1991

#### Electrophotographic photoconductor

INVENTOR: Kojima, Narihito, Numazu, Japan  
Nagame, Hiroshi, Numazu, Japan  
Seto, Mitsuru, Yamakita, Japan  
Yamazaki, Shunpei, Atsugi, Japan  
Hayashi, Shigenori, Atsugi, Japan  
Ishida, Noriya, Atsugi, Japan  
Hirose, Naoki, Atsugi, Japan  
Sasaki, Mari, Atsugi, Japan  
Takeyama, Junichi, Atsugi, Japan

... [\*16] 1, wherein the Vickers hardness of said organic photoconductive layer is 10 to 50  $\text{Kg/mm}^2$  .

[\*17] 17. The electrophotographic photoconductor as claimed in claim 1, wherein organic photoconductive layer is a single-layer-type photoconductive layer.

[\*18] 18. The electrophotographic photoconductor as claimed in claim 17, wherein the thickness of said single-layer-type photoconductive layer is 5 to 30  $\mu\text{m}$ .

[\*19] 19. The electrophotographic photoconductor as claimed in claim 1, wherein organic photoconductive layer is a function-separated-type photoconductive layer comprising a ...

LEVEL 1 - 76 OF 225 PATENTS

5,054,134

<=2> GET 1st DRAWING SHEET OF 5

Oct. 8, 1991

#### Upper layer water flow type circulating water pool

INVENTOR: Teratsuji, Osamu, Ichikawa, Japan  
Nishimura, Keiichi, Urawa, Japan

PAGE 83

Moriya, Yoshiro, Matsudo, Japan  
Ueda, Yukihiko, Yokohama, Japan

What is claimed is:

[\*1] 1. An upper water flow layer type circulating water pool comprising a circulating pool main body with front and rear curved portions; a swimming tank or pool defined by an opening in an upper portion of said circulating ...

PAGE 84

LEVEL 1 - 77 OF 225 PATENTS

5,051,126

<=2> GET 1st DRAWING SHEET OF 1

Sep. 24, 1991

Cermet for tool

INVENTOR: Yasui, Hajime, Nagoya, Japan  
Suzuki, Junichiro, Hashima, Japan

... [\*1] layer is composed of more transitional metals selected from the group consisting of the group IVb metals than the core, and the core is composed of more transitional metals selected from the group consisting of the group Vb metals and tungsten than any outer layer of the Type-II particles.

[\*2] 2. The cermet of claim 1, wherein the ratio of transitional metals in group IVb, transitional metals in group Vb, and tungsten to carbon and nitrogen is 1.0:0.85-1.0.

[\*3] 3. The cermet of claim ...

LEVEL 1 - 78 OF 225 PATENTS

5,050,323

<=2> GET 1st DRAWING SHEET OF 2

Sep. 24, 1991

Badge

INVENTOR: Gagnon, Raymond, Montreal, Canada

... [\*1] front face of said body layer, and

fastening means carried by the back face of said body layer to attach said body layer to a wearer's clothing; wherein:

the foam material forming the body layer is of the type having no memory when compressed;

PAGE 85

said foam material is left exposed at the peripheral edge of said body layer; and,

said badge further comprises a protecting transparent film covering said image-bearing ...

... [\*9] front face of said body layer; and,

fastening means carried by the back face of said body layer to attach said body layer to a wearer's clothing; wherein:

the expanded polystyrene forming the body layer is of the type having no memory when compressed;

said expanded polystyrene is left exposed at the peripheral edge of said body layer; and,

said badge further comprises a protecting transparent film covering said image-bearing ...

... [\*10] front face of said body layer; and,

fastening means carried by the back face of said body layer to attach said body layer to a wearer's clothing, wherein;

the expanded polystyrene forming the body layer is of the type having no memory when compressed;

said expanded polystyrene is left exposed at the peripheral edge of said body layer; and,

said badge further comprises a protecting transparent film covering said image-bearing ...

LEVEL 1 - 79 OF 225 PATENTS

5,039,627

<=2> GET 1st DRAWING SHEET OF 7

Aug. 13, 1991

Method of producing a quasi-flat semiconductor device  
capable of a multi-wavelength laser effect and the  
corresponding device

INVENTOR: Menigaux, Louis, Bures sur Yvette, France.  
Dugrand, Louis, Chelles, France

... [\*4] least one material selected from the group consisting of aluminum, gallium and indium and at least one material selected from the group consisting of phosphorous, arsenic and antimony.



[\*5] 5. A method according to claim 4, wherein the active layers are of type N, and comprise Ga 1 - x Al x As, x differing each time, and being less than approximately 10%, while the confining layers comprise Ga 1 - y Al y ...

... [\*9] about one-tenth of a micron.

[\*10] 10. A method according to claim 1, wherein the upper layer is a group III-V alloy.

[\*11] 11. A method according to claim 5, wherein the upper layer is type P gallium arsenide.

[\*12] 12. A method according to claim 1, wherein said levelling comprises an erosion operation applied to the upper surface of the block, laying bare at least over the major part of the eroded ...

... [\*30] least one material selected from the group consisting of aluminum, gallium and indium and at least one material selected from the group consisting of phosphorous, arsenic and antimony.

[\*31] 31. A method according to claim 30, wherein the active layers are of type N, and comprises Ga 1 - x Al x As, x differing each time and being less than approximately 10%, while the confinement layers comprise Ga 1 - y Al y ...  
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LEVEL 1 - 80 OF 225 PATENTS

5,037,505

<=2> GET 1st DRAWING SHEET OF 2

Aug. 6, 1991

Construction process for a self-aligned transistor

INVENTOR: Tung, Pham N., Paris, France

... [\*2] mask,

i) dissolving the two silica masks in a solution of HF + NH4F + H2O.

[\*3] 3. Process of constructing a self-aligned transistor, according to claim 1, from a substrate comprising layers of type N and N< + > formed by epitaxy, further comprising the steps of:

a) depositing and masking by a first resin mask creating a resin pattern of dimensions corresponding to the power of resolution of said ...

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LEVEL 1 - 81 OF 225 PATENTS

5,031,025

<=2> GET 1st DRAWING SHEET OF 3

Jul. 9, 1991

Hermetic single chip integrated circuit package

INVENTOR: Braun, Robert E., Norristown, Pennsylvania  
Gibbs, Ronald T., King of Prussia, Pennsylvania

... [\*1] said rim of said lid being sealed to said substrate, thereby forming an hermetic package.

[\*2] 2. An hermetic integrated circuit package as defined in claim 1 wherein said wiring substrate is of the multi-layer type, said lead terminals being coupled to said input/output terminals.

[\*3] 3. An hermetic integrated circuit package as defined in claim 2 wherein said rim of said lid is comprised of a ...  
LEVEL 1 - 82 OF 225 PATENTS

5,028,786

<=2> GET 1st DRAWING SHEET OF 4

Jul. 2, 1991

Array for a nuclear radiation and particle detector

INVENTOR: Da Silva, Angela J., Vancouver, Canada  
Le Gros, Mark A., Vancouver, Canada  
Turrell, Brian G., Vancouver, Canada  
Kotlicki, Andrzej, Warsaw, Maryland, Poland  
Drukier, Andrzej K., Greenbelt, Maryland

... [\*13] detector as defined in claim 8 wherein said each array is a planar array.

[\*14] 14. A method of making a detector array comprising depositing a substantially continuous film layer of type I superconducting material on a substrate removing a portion of said film to leave a plurality of discrete pixels each of a predetermined size of said type I superconducting material arranged ...

LEVEL 1 - 83 OF 225 PATENTS

5,028,505

Jul. 2, 1991

Electrophotographic photoreceptor

INVENTOR: Akasaki, Yutaka, Kanagawa, Japan  
Nukada, Katsumi, Kanagawa, Japan  
Sato, Katsuhiro, Kanagawa, Japan

... [\*9] comprising a compound of formula (I), (II), or (III) as set forth in claim 1.

[\*10] 10. The electrophotographic photoreceptor as claimed in claim 1, wherein the photosensitive layer is of a single layer type.

PAGE

91

LEVEL 1 - 84 OF 225 PATENTS

5,024,913

Jun. 18, 1991

Electrophotographic photosensitive material

INVENTOR: Yoshida, Takeshi, Kawachinagano, Japan  
Nakatani, Kaname, Osaka, Japan  
Fukami, Toshiyuki, Sakai, Japan  
Tanaka, Nariaki, Kishiwada, Japan

... [\*6] photosensitive layer.

[\*7] 7. The electrophotographic photosensitive material of claim 6, wherein the surface protective layer is 2 to 5 microns thick.

[\*8] 8. The electrophotographic photosensitive material of claim 1, wherein the photosensitive layer is of a single layer type.

[\*9] 9. The electrophotographic photosensitive material of claim 8, wherein the photosensitive layer is 10 to 50 microns thick.

[\*10] 10. The electrophotographic photosensitive material of claim 8, wherein the photosensitive layer is 15 to 25 microns thick.

[\*11] 11. The ...

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LEVEL 1 - 85 OF 225 PATENTS

5,022,441

<=2> GET 1st DRAWING SHEET OF 67

Jun. 11, 1991

Papermaker's double layer fabric with high warp and weft  
volume per repeat

INVENTOR: Tate, Takuo, Hachioji, Japan  
Watanabe, Taketoshi, Inagi, Japan  
Nagura, Hiroyuki, Inagi, Japan

What is claimed is:

[\*1] 1. A papermakers' double layer type fabric comprising in one repeat a warp layer, said warp layer having an upper surface and a lower surface, said warp layer consisting of  $n \times 2$  of warps wherein  $n$  is an ...

... [\*1] being each interlaced once in one repeat with a warp, wherein said lower surface polyamide wefts are of larger diameter than said lower surface polyester wefts.

[\*2] 2. A papermakers' double layer type fabric comprising in one repeat a warp layer, said warp layer having an upper surface and a lower surface, said warp layer consisting of  $n \times 2$  of warps wherein  $n$  is an ...

... [\*2] between which said non-interlacing warp is located to form a knuckle so that the knuckles so formed on each of the adjacent lower surface wefts are arranged in a staggered relation.

[\*3] 3. A papermakers' double layer type fabric according to claim 2, wherein a non-interlacing warp sandwiched in between a pair of warps interlacing with a lower surface polymeric weft, interlaces with an upper surface weft at a position where said pair of warps interlace with the lower surface polymeric weft.

[\*4] 4. A papermakers' double layer type fabric according to claim 2, wherein in said  $n \times 2$  of warps, a non-interlacing warp and a warp interlacing with a lower surface polymeric weft, are alternately arranged.

[\*5] 5. A papermakers' double layer type fabric according to claim 2, wherein in said  $n \times 2$  of warps, a non-interlacing warp and a plurality of warps interlacing with a lower surface polymeric weft, are alternately arranged.

[\*6] 6. A papermakers' double layer type fabric according to claim 2, wherein said lower surface polyamide wefts are of larger diameter than said lower surface polyester wefts.

[\*7] 7. A papermakers' double layer type fabric comprising in one repeat a warp layer, said warp layer having an upper surface and a lower surface, said warp layer consisting of  $n \times 2$  of warps, wherein  $n$  is an ...

... [\*7] each interlaced once in one repeat with a warp and the lower surface polyester wefts being each interlaced twice in one repeat with a warp.

PAGE 93

Pat. No. 5022441, \*7

[\*8] 8. A papermakers' double layer type fabric according to claim 7, wherein said lower surface polyamide wefts are of larger diameter than said lower surface polyester wefts.

[\*9] 9. A papermakers' double layer type fabric according to claim 7, wherein the number of said lower surface polyamide wefts and that of said lower surface polyester wefts are in a ratio of from 1:3 to 3:1.

- [\*10] 10. A papermakers' double layer type fabric according to claim 7, wherein both said lower surface polyamide wefts and lower surface polyester wefts are each interlaced with two adjacent warps.
- [\*11] 11. A papermakers' double layer type fabric according to claim 10, wherein said lower surface polyamide wefts are of larger diameter than said lower surface polyester wefts.
- [\*12] 12. A papermakers' double layer type fabric according to claim 10, wherein the number of said lower surface polyamide wefts and that of said lower surface polyester wefts are in a ratio of from 1:3 to 3:1.
- [\*13] 13. A papermakers' double layer type fabric according to claim 7, wherein said lower surface polyester wefts are each interlaced twice in one repeat with a warp, and said lower surface polyamide wefts are each interlaced once ...
- ... [\*13] pair of adjacent warps between which a warp interlacing with an upper surface weft at a position where said pair of warps interlace with the lower surface polyamide weft, is disposed.
- [\*14] 14. A papermakers' double layer type fabric according to claim 13, wherein a non-interlacing warp is arranged adjacent to a warp interlacing with said lower surface polyester weft.
- [\*15] 15. A papermakers' double layer type fabric according to claim 13, wherein at least one of a pair of warps which interlace with said lower surface polyamide weft also interlaces with the lower surface polyester weft.
- [\*16] 16. A papermakers' double layer type fabric according to claim 13, wherein said lower surface polyamide wefts are of larger diameter than said lower surface polyester wefts.
- [\*17] 17. A papermakers' double layer type fabric according to claim 13, wherein the number of said lower surface polyamide wefts and that of said lower surface polyester wefts are in a ratio of 1:3 to 3:1.
- [\*18] 18. A papermakers' double layer type fabric according to claim 13, wherein said lower surface polyamide wefts are each interlaced once in one repeat with a pair of adjacent warps between which a warp interlacing with an upper surface ...
- ... [\*18] polyester wefts are each interlaced twice in one repeat with a warp located between a pair of warps interlacing with a lower surface polyamide weft.
- [\*19] 19. A papermakers' double layer type fabric according to claim 18, wherein said lower surface polyamide wefts are of larger diameter than said lower surface polyester wefts.

[\*20] 20. A papermakers' double layer type fabric according to claim 18, wherein the number of said lower surface polyamide wefts and that of said lower surface polyester wefts are in a ratio of from 1:3 to 3:1.

PAGE

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LEVEL 1 - 86 OF 225 PATENTS

5,005,057

<=2> GET 1st DRAWING SHEET OF 19

Apr. 2, 1991

Semiconductor light-emitting diode and method of  
manufacturing the same

INVENTOR: Izumiya, Toshihide, Tokyo, Japan  
Ohba, Yasuo, Yokohama, Japan  
Hatano, Aki, Tokyo, Japan

... [\*7] conductivity type having a zinc blend type crystal structure.

[\*8] 8. A diode according to claim 3 or 7, wherein said light-reflection layer has a multilayered structure in which said superlattice layers of the types are alternately stacked with a period which is substantially equal to the light-emitting wavelength.

[\*9] 9. A semiconductor light-emitting diode including a light-emitting layer having a p-n junction, comprising:

...

LEVEL 1 - 87 OF 225 PATENTS

4,996,108

<=2> GET 1st DRAWING SHEET OF 9

Feb. 26, 1991

Sheets of transition metal dichalcogenides

INVENTOR: Divigalpitiya, W. M. Ranjith, Vancouver, Canada  
Frindt, Robert F., Vancouver, Canada  
Morrison, S. Roy, Burnaby, Canada

What is claimed is:

[\*1] 1. A process for forming sheet-like compositions of the formula:

MX<sub>2</sub>:Y

wherein MX<sub>2</sub> is a layer-type transition metal dichalcogenide, M is a metal selected from the group consisting of niobium, tantalum, molybdenum and

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tungsten, X is a chalcogen selected from the group consisting of sulfur and selenium and Y is a material located ...

... [\*18] A method of coating an object, comprising:

forming a sheet-like composition at an interface between water and a non-metallic liquid which is immiscible with water, the composition having the formula:

MX2:Y

wherein MX2 is a layer-type transition metal dichalcogenide, the M is selected from the group consisting of niobium, tantalum, molybdenum and tungsten; X is selected from the group consisting of sulfur and selenium, and Y is a material located between layers of MX2; and

bringing the ...

... [\*18] spread over the object.

[\*19] 19. A method as claimed in claim 18, wherein the MX2 is crystalline with c-axes perpendicular to the substrate.

[\*20] 20. A composition having the formula:

MX2:Y

wherein MX2 is a layer-type transition metal dichalcogenide selected from the group consisting of molybdenum disulfide and tungsten disulfide; and Y is an

PAGE 97

Pat. No. 4996108, \*20

organic material located between layers of MX2.

[\*21] 21. A composition as claimed in claim 20, wherein the ...

... [\*24] tetrachloride; dimethoxy benzene; 1-chloronaphthalene; chrysene; stearamide; phthalocyanine; copper phthalocyanine and iron pentacarbonyl.

[\*25] 25. A object having a surface coated with a composition having the formula:

MX2:Y

wherein MX2 is a layer-type transition metal dichalcogenide, M is a metal selected from the group consisting of niobium, tantalum, molybdenum and tungsten, X is a chalcogen selected from the group consisting of sulfur and selenium, and Y is an organic substance located ...

LEVEL 1 - 88 OF 225 PATENTS

4,980,313

Dec. 25, 1990

Method of producing a semiconductor laser

INVENTOR: Takahashi, Shogo, Itami, Japan

What is claimed is:

- [\*1] 1. A method of producing a semiconductor laser comprising:  
growing at least a p type lower cladding layer, a quantum well active layer, and an n type upper cladding layer successively on a substrate;  
depositing a first film as a source for diffusion of n type impurities on a portion of the n type upper cladding layer;

...

LEVEL 1 - 89 OF 225 PATENTS

PAGE 99

4,980,216

Dec. 25, 1990

Transfer for textiles

INVENTOR: Rompp, Walter, Rosenstrasse 46, D-7406 Mossingen, Federal Republic of Germany

... [\*10] freely cross-linkable silicon emulsion.

[\*11] 11. A transfer according to claim 10, wherein said separating layer is a polysiloxane compound.

[\*12] 12. A transfer according to claim 1, wherein said separating layer is of the type C1G 2 pure.

[\*13] 13. A transfer according to claim 1, wherein said separating layer is screen-printable.

[\*14] 14. A transfer according to claim 1, wherein said separating layer is manufactured on a ...

LEVEL 1 - 90 OF 225 PATENTS

PAGE 100

4,976,990

Dec. 11, 1990

Process for metallizing non-conductive substrates



INVENTOR: Bach, Wolf, Southbury, Connecticut  
Ferrier, Donald R., Thomaston, Connecticut  
Kukanskis, Peter E., Woodbury, Connecticut  
Williams, Ann S., Southbury, Connecticut  
Senechal, Mary J., Canton, Connecticut

... [\*3] electroless depositing solution to deposit metal fully and adherently and essentially void-free onto said catalyzed through-hole surfaces.

[\*4] 4. In a process for manufacturing printed circuit boards of the multi-layer type, in which a planar composite substrate material is provided comprised of a laminate of alternating parallel layers of metal and non-conductive, glass-reinforced thermosetting or thermoplastic material, and in which through-holes are provided ...

... [\*4] metal depositing solution to deposit metal fully and adherently and essentially void-free onto said catalyzed through-hole surfaces.

[\*5] 5. In a process for manufacturing printed circuit boards of the multi-layer type, in which a planar composite substrate material is provided comprised of a laminate of alternating parallel layers of metal and non-conductive, glass-reinforced thermosetting or thermoplastic material, and in which through-holes are provided ...

... [\*11] time of said process for metallizing said through-hole surfaces.

[\*12] 12. A process for providing metallized through-holes in a printed circuit board of the double-sided or multi-layer type, comprising the steps of:

(a) providing a printed circuit substrate material comprised of a member selected from the group consisting of (1) a planar non-conductive material comprised of glass-reinforced thermosetting or ...

... [\*12] metal depositing solution to deposit metal fully and adherently and essentially void-free onto said catalyzed through-hole surfaces.

[\*13] 13. The process according to claim 12 wherein said printed circuit board is of the multi-layer type and wherein said through-hole surfaces are desmeared between steps (b) and (c).

[\*14] 14. A process for providing a full-coverage, essentially void-free, adherent metal layer on the surface of a ...

LEVEL 1 - 91 OF 225 PATENTS

4,963,450

Oct. 16, 1990

Electrophotographic photosensitive member with disazo pigment

INVENTOR: Miyazaki, Hajime, Yokohama, Japan  
Go, Shintetsu, Yokohama, Japan  
Senoo, Akihiro, Yokohama, Japan  
Iuchi, Kazushi, Yokohama, Japan  
Kanemaru, Tetsuro, Tokyo, Japan

What is claimed is:

[\*1] 1. A laminated layer type electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive support, characterized in that the charge generation layer has at least one of disazo pigments [is by] of the formulae (1) and ( ...

PAGE 102

LEVEL 1 - 92 OF 225 PATENTS

4,941,737

<=2> GET 1st DRAWING SHEET OF 5

Jul. 17, 1990

Liquid-crystal display device using twisted nematic liquid crystal molecules

INVENTOR: Kimura, Naofumi, Nara, Japan

What is claimed is:

[\*1] 1. A liquid-crystal display device comprising:

a multi-layer-type liquid-crystal cell that is composed of at least first and second cell layers, said cell layers containing liquid-crystal molecules with a twisted nematic orientation therein;

said first cell layer having an angle of ...

LEVEL 1 - 93 OF 225 PATENTS

4,932,788

<=2> GET 1st DRAWING SHEET OF 4

Jun. 12, 1990

Monitoring of the quality of a flowing vapor

INVENTOR: Yeh, George C., 2 Smedley Dr., Newtown Square, Pennsylvania 19073

... [\*5] 1 wherein said flowmeter is a mass flowmeter capable of directly metering the mass flow rate of the vaporized sample.

[\*6] 6. A system according to claim 5 wherein said mass flowmeter is of an electrothermal boundary-layer type flowmeter in which temperature sensing and

heating elements are placed outside the pipe carrying said stream of sample vapor and do not obstruct the stream.

[\*7] 7. A system according to claim 1 wherein said means ...

... [\*16] said heater means further comprises:

a thermal insulator completely covering said shell and the inlet and outlet thereof.

[\*17] 17. Apparatus according to claim 11 wherein said mass flowmeter means is of the electrothermal boundary-layer type for permitting unobstructed flow.

[\*18] 18. Apparatus according to claim 11 wherein said second sensing means comprises:

thermistors formed into thin bands and placed around the inlet and outlet of said heater means.

[\*19] ...

LEVEL 1 - 94 OF 225 PATENTS

4,888,261

<=2> GET 1st DRAWING SHEET OF 5

Dec. 19, 1989

Electrophotographic photosensitive member

INVENTOR: Mabuchi, Minoru, Tokyo, Japan

... [\*6] electrophotographic photosensitive member of claim 1, wherein said charge transport layer is laminated on said charge generation layer.

[\*7] 7. The electrophotographic photosensitive member of claim 1, wherein said photosensitive layer has a single layer type that the charge-generating material and the charge-transporting material are contained in the same layer.

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LEVEL 1 - 95 OF 225 PATENTS

4,886,721

<=2> GET 1st DRAWING SHEET OF 10

Dec. 12, 1989

Electrophotographic plate by use of metal naphthalocyanine derivative

INVENTOR: Hayashida, Shigeru, Hitachi, Japan  
Tai, Seiji, Hitachi, Japan

Hayashi, Nobuyuki, Hitachi, Japan  
Iwakabe, Yasushi, Hitachi, Japan  
Kinjo, Noriyuki, Hitachi, Japan  
Numata, Shunichi, Hitachi, Japan

... [\*3] germaniumnaphthalocyanine,  
bis(tripropylsiloxy)germaniumnaphthalocyanine,  
bis(tributylsiloxy)germaniumnaphthalocyanine,  
bis(triphenylsiloxy)germaniumnaphthalocyanine and  
bis(triethylsiloxy)tinnaphthalocyanine.

[\*4] 4. The electrophotographic plate according to claim 1, wherein said photoconductive layer is a complex double layer type comprising a charge generation layer containing said metal naphthalocyanine derivative which is a charge generation substance, and said charge transport layer containing a charge transport substance.

[\*5] 5. The electrophotographic ...  
LEVEL 1 - 96 OF 225 PATENTS

4,877,702

Oct. 31, 1989

Electrophotographic sensitive material

INVENTOR: Miyamoto, Eiichi, Osaka, Japan  
Mutou, Nariaki, Daito, Japan  
Nakazawa, Tooru, Osaka, Japan

What is claimed is:

[\*1] 1. An electrophotographic sensitive material provided with a single-layer type sensitive layer containing an electric charge generating substance, an electric charge transferring substance, and a binding resin, characterized in that said electric charge generating substance is a perylene type compound ...

LEVEL 1 - 97 OF 225 PATENTS

4,867,827

Sep. 19, 1989

Process for gold foil stamping in relief

INVENTOR: Lesieur, Frederic, 25, Rue Pradier, Paris, France 75019

I claim:



[\*1] 1. A method of gilding raised images formed by a thermographic process on a substrate with a marking layer of the type releasably disposed on a backing film comprising the steps of:

providing a thermally activated adhesive powder of the type that exhibits adhesive properties while in a solidified state;

printing a selected ...

... [\*9] percentage basis, of 65% styrene oleophthalic resin; 15% to 20% acrylic resin; 10% to 15% plasticizer; 5% to 10% microcrystalline wax.

[\*10] 10. A method of gilding a substrate with a marking layer of the type releasably disposed on a backing film, comprising the steps of:

providing a thermally activated adhesive powder of the type that will liquefy under a sufficient amount of heat and will exhibit adhesive properties when ...

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LEVEL 1 - 98 OF 225 PATENTS

4,852,593

<=2> GET 1st DRAWING SHEET OF 2

Aug. 1, 1989

Lubrication monitoring apparatus for machine

INVENTOR: Nakajima, Yoshiaki, Yono, Japan  
Suzuki, Tadashi, Machida, Japan  
Wada, Yoneji, Urawa, Japan

... [\*4] a separate pump and supplied to said lubricated mechanical section.

[\*5] 5. A lubrication monitoring apparatus for a machine as claimed in claim 1, wherein said filter is a deep-layer type filter.

[\*6] 6. A lubrication monitoring apparatus for a machine as claimed in claim 1, wherein said warning device is connected with a recorder to make a recording when difference in ...

LEVEL 1 - 99 OF 225 PATENTS

4,822,590

<=2> GET 1st DRAWING SHEET OF 3

Apr. 18, 1989

Forms of transition metal dichalcogenides

INVENTOR: Morrison, S. Roy, Burnaby, Canada  
Frindt, Robert F., Vancouver, Canada  
Joensen, Per, Coquitlam, Canada  
Gee, Michael A., Vancouver, Canada  
[Miremadi, Bijan K., Coquitlam, Canada]

We claim:

[\*1] 1. An exfoliation process for preparing a single layer substance of the form

MX 2

wherein MX2 is a layer type transition metal dichalcogenide selected from the group consisting of MoS<sub>2</sub>, TaS<sub>2</sub>, WS<sub>2</sub>, which comprises:

(a) intercalating multi-layer MX2 with an alkali metal in a dry environment for sufficient time to enable the ...

LEVEL 1 - 100 OF 225 PATENTS

4,800,568

<=2> GET 1st DRAWING SHEET OF 1

Jan. 24, 1989

Gas laser with a frequency-selective dielectric layer system

INVENTOR: Krueger, Hans, Munich, Federal Republic of Germany  
Good, Hans P., Sargans, Switzerland

... [\*1] said means being a frequency selective layer system being formed on the Brewster window, said system comprising:

a plurality of successive layers, said plurality of layers including only two layer types and including alternating high refractive index first layers and low refractive index second layers, each of said first layers having substantially a first optical thickness and each of said second layers having ...

... [\*9] opposite ends through which laser radiation is emitted, an improved frequency selective layer system comprising:

a plurality of successive layers on said Brewster window, said plurality of layers including only two layer types and including alternating high refractive index first layers and low refractive index second layers, each of said first layers having substantially a thickness of 71.2 nm and each of said second layers having ...

LEVEL 1 - 101 OF 225 PATENTS

4,790,954

PAGE 111

PAGE 110

Dec. 13, 1988

Mixed metal hydroxide-clay adducts as thickeners for water  
and other hydrophylic fluids

INVENTOR: Burba, III, John L., Angleton, Texas  
Barnes, Audrey L., Lake Jackson, Texas

... [\*16] saconite, vermiculite, chlorite, attapulgite, sepiolite,  
palygorskite, and Fullers' earth.

[\*17] 17. The method of claim 1 wherein the mineral clay is at least one of  
the group consisting of amorphous clays of the allophane group and crystalline  
clays of the 2-layer type, 3-layer type, expanding type, non-expanding type,  
elongate type, regular mixed layer type, and chain structure type.

[\*18] 18. The method of claim 1 wherein the mineral clay is bentonite.

[\*19] 19. The method of claim 1 wherein the mineral clay is beneficiated  
bentonite.

[\*20] 20. The method of claim 1 wherein the weight ratio of monolayered ...

PAGE 112

LEVEL 1 - 102 OF 225 PATENTS

4,775,814

<=2> GET 1st DRAWING SHEET OF 3

Oct. 4, 1988

Saw device

INVENTOR: Yuhara, Akitsuna, Kawasaki, Japan  
Sasaki, Jun, Sagami-hara, Japan  
Hirashima, Tetsuya, Yokohama, Japan  
Yamada, Jun, Yokohama, Japan

... [\*16] substrate and sets of finger electrodes disposed on said  
substrate, at least one set of said electrodes having a laminated structure made  
up of a plurality of layers including at least one of a first layer type of an  
aluminum film and at least one of a second layer type of an aluminum film which  
includes an impurity selected from the group consisting of titanium, chromium,  
vanadium and manganese.

[\*17] 17. A SAW device according to claim 16, wherein said laminated  
structure includes a first layer of said first layer type formed on said  
substrate and a second layer of said second layer type formed on said first  
layer, the thickness of said first layer being greater than the thickness of  
said second layer.



[\*18] 18. A SAW device according to claim 16, wherein said laminated structure includes a first layer of said second layer type formed on said substrate and a second layer of said first layer type formed on said first layer, the thickness of said second layer being greater than the thickness of said first layer.

[\*19] 19. A SAW device according to claim 16, wherein said laminated structure includes a first layer of said first layer type formed on said substrate, a second layer of said second layer type formed on said first layer, and a third layer of said first layer type formed on said second layer, the combined thickness of said first and third layers being greater than the thickness of said second layer.

[\*20] 20. A SAW device according to claim 16, wherein said laminated structure includes a first layer of said second layer type formed on said substrate, a second layer of said first layer type formed on said first layer, and a third layer of said second layer type formed on said second layer, the thickness of said second layer being greater than the combined thickness of said first and third layers.

[\*21] 21. A SAW device according to claim 16, wherein said laminated structure includes a first layer of said first layer type formed on said substrate, a second layer of said second layer type formed on said first layer, a third layer of said first layer type formed on said second layer, and a fourth layer of said second layer type formed on said third layer, the combined thickness of said first and third layers being greater than the combined thickness of said second and fourth layers.

Pat. No. 4775814, \*21

[\*22] 22. A SAW device according to claim 17, wherein said first layer type includes an impurity selected from the group consisting of titanium, copper, magnesium, zinc and nickel.

[\*23] 23. A SAW device according to claim 22, wherein said first layer includes first and second sublayers having different ...

LEVEL 1 - 103 OF 225 PATENTS

4,773,074

<=2> GET 1st DRAWING SHEET OF 2

Sep. 20, 1988

Dual mode laser/detector diode for optical fiber transmission lines

INVENTOR: Hunsperger, Robert G., Newark, Delaware  
Park, Jung H., Newark, Delaware

... [\*12] conductivity type of the active layer, the waveguide layer having first and second surfaces, the first surface in contact with the second surface of the active layer;

a confining layer having a conductivity layer opposite the active layer type and having a surface in contact with the second surface of the waveguide layer;

cap and substrate layers; and

means to couple the cell and optical and electrical circuits.

AGE 115

LEVEL 1 - 104 OF 225 PATENTS

4,761,242

<=2> GET 1st DRAWING SHEET OF 2

Aug. 2, 1988

Piezoelectric ceramic composition

INVENTOR: Suzuki, Kazunori, Nagoya, Japan  
Naitoh, Masataka, Kariya, Japan

... [\*14] constant-temperature characteristic, said additive being selected from the group consisting of 10-55 mol % CaTiO<sub>3</sub> and 1-15 mol % SrTiO<sub>3</sub>, and

the balance of the composition being PbBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> having a Bi-layer type structure which PbBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> has a positive dielectric constant-temperature characteristic,

a change in the dielectric constant of the PbBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> which change occurs by a change in temperature being substantially compensated for ...

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LEVEL 1 - 105 OF 225 PATENTS

4,753,187

<=2> GET 1st DRAWING SHEET OF 4

Jun. 28, 1988

Individual submarine diving equipment

INVENTOR: Galimand, Patrice, Paris, France

... [\*10] tightness and passage of electric connection between the container and the motor are provided.

[\*11] 11. The device of claim 1, comprising a control for the motor realized by a moulding-on of a contactor of the deformable thin layer type, said moulding-on having the form of a buckle portion completed by a strip having

pressure connecting means for connection around a hand of the diver, the buckle element being disposable around the diver's ...

PAGE 117

LEVEL 1 - 106 OF 225 PATENTS

4,729,459

<=2> GET 1st DRAWING SHEET OF 9

Mar. 8, 1988

Adjustable damping force type shock absorber

INVENTOR: Inagaki, Mitsuo, Okazaki, Japan  
Sasaya, Hideaki, Okazaki, Japan  
Takeda, Kenji, Aichi, Japan  
Nakano, Hiromichi, Okazaki, Japan  
Kamiya, Sigeru, Aichi, Japan  
Ishida, Toshinobu, Okazaki, Japan

... [\*1] said plunger to that of said other end surface of said sliding member.

[\*2] 2. An adjustable damping force type shock absorber according to claim 1, wherein said piezo-electric body is a lamination layer type piezo-electric body constituted by laminating in an axial direction a plurality of piezo-electric elements having a piezo-electric effect in which application of a stress in the axial direction ...

... [\*4] piezo-electric body on the basis of the electric signal from the damping force sensor.

[\*5] 5. An adjustable damping force type shock absorber according to claim 4, wherein said piezo-electric body is a lamination layer type piezo-electric body constituted by laminating a plurality of piezo-electric elements.

[\*6] 6. An adjustable damping force type shock absorber according to claim 5, wherein said lamination layer type piezo-electric body comprises electrode plates inserted between adjacent piezo-electric elements and forming, respectively, a first electrode by connecting alternate electrode plates in parallel and a ...

LEVEL 1 - 107 OF 225 PATENTS

4,723,601

Feb. 9, 1988

Multi-layer type heat exchanger

INVENTOR: Ohara, Toshio, Kariya, Japan  
Tsuchiya, Kiyomitsu, Okazaki, Japan  
Kittaka, Kiyoshi, Aichi, Japan  
Sudo, Yasuhiro, Okazaki, Japan

PAGE 118

Yamauchi, Yoshiyuki, Aichi, Japan  
Miyata, Yoshio, Nagoya, Japan

What is claimed is:

[\*1] 1. A multi-layer type heat exchanger including:

a row of a plurality of substantially parallel flat tubes each formed by two core plates prepared by press work and sealingly jointed together;

each ...

... [\*7] one outermost core plate to assure that said protecting plate is spaced from said one outermost core plate a distance sufficient to accommodate said further corrugated fin.

[\*8] 8. A multi-layer type heat exchanger including:

a row of a plurality of substantially parallel flat tubes each formed by two core plates prepared by press work and sealingly jointed together;

each ...

LEVEL 1 - 108 OF 225 PATENTS

4,703,266

<=2> GET 1st DRAWING SHEET OF 4

Oct. 27, 1987

Gradient meter with thin magnetic layer

INVENTOR: Chiron, Guy, Gieres, France  
Dumont, Andre , St. Egreve, France

... [\*1] meter to measure the spatial derivatives

delta  $H_i / \delta x_j$  ( $i = x, y, z; j = x, y, z$ )

of a magnetic field H utilizing magnetic sonds with a thin layer of the type which comprises:

a magnetic layer of cylindrical form of revolution, the magnetic layer having an axis of difficult magnetization parallel to the axis of the cylinder and an axis of easy magnetization that is circular in a plane of the layer in a ...

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LEVEL 1 - 109 OF 225 PATENTS

4,702,019

<=2> GET 1st DRAWING SHEET OF 7

Oct. 27, 1987

Apparatus for cooling high-temperature particles

INVENTOR: Tsuruno, Masayoshi, Funabashi, Japan  
Horie, Michihiko, Nagareyama, Japan

... [\*1] said guide tube and is vertically reciprocable so that displacement in the radially outward directions of said high-temperature particles along an outer surface of said conical or pyramidal body is facilitated, and a second packed layer type cooling zone disposed below said first cooling zone for gradually cooling said high-temperature particles while said high-temperature particles which have been rapidly cooled in said first ...

PAGE 121

LEVEL 1 - 110 OF 225 PATENTS

4,696,548

<=2> GET 1st DRAWING SHEET OF 7

Sep. 29, 1987

Antiglare mirror for an automobile

INVENTOR: Ueno, Yoshiki, Okazaki, Japan  
Taguchi, Takasi, Anjo, Japan  
Hattori, Tadashi, Okazaki, Japan

... [\*1] selected thickness, so that light reflecting from said mirror and passing through said first dielectric layer has desired color characteristics.

[\*2] 2. A mirror arrangement according to claim 1, wherein said liquid crystal layer is of the type whose transparency is reduced when an electric field is applied thereto compared to that when an electric field is not applied thereto.

[\*3] 3. A mirror arrangement according to claim 1, further comprising: a second transparent dielectric layer located on the ...

LEVEL 1 - 111 OF 225 PATENTS

4,686,159

<=2> GET 1st DRAWING SHEET OF 3

Aug. 11, 1987

Laminated layer type fuel cell

INVENTOR: Miyoshi, Hideaki, Kobe, Japan

What is claimed is:

[\*1] 1. A laminated layer type fuel cell for converting electrochemical reaction of fuel and oxidizer into electric power, said fuel cell comprising a plurality of gas separation plates, each having rectilinear and zigzag portions of fuel and oxidizer ...

... [\*1] electrolyte matrix, and an oxidizer electrode whereby partial pressures of reaction gases produced by the electrochemical reaction are equalized throughout the cell to equalize cell reactions and temperature distribution in the cell.

[\*2] 2. A laminated layer type fuel cell as claimed in claim 1 wherein the rectilinear and zigzag portions of fuel and oxidizer channels have a length ratio of 1:1 and the zigzag portions are alternately disposed at upstream and downstream sides of the reaction gases.

[\*3] 3. A laminated layer type fuel cell as claimed in claim 1 wherein the rectilinear and zigzag portions of fuel and oxidizer channels have a length ratio of 2:1 to 4:1 and the zigzag portions are sequentially displaced with respect to each channel.

LEVEL 1 - 112 OF 225 PATENTS

4,673,591

Jun. 16, 1987

Production of layer-type magnetic recording media

INVENTOR: Lehner, August, Roedersheim-Gronau, Federal Republic of Germany  
Heil, Guenter, Ludwigshafen, Federal Republic of Germany  
Lenz, Werner, Bad Dürkheim, Federal Republic of Germany  
Balz, Werner, Limburgerhof, Federal Republic of Germany  
Kohl, Albert, Laumersheim, Federal Republic of Germany  
Schornick, Gunnar, Neuleiningen, Federal Republic of Germany

We claim:

[\*1] 1. A process for the production of a layer-type magnetic recording medium by dispersing a finely divided magnetically anisotropic material in a binder which consists of not less than 30% of a radiation-curable aqueous binder dispersion, applying the ...

LEVEL 1 - 113 OF 225 PATENTS

4,671,969

Jun. 9, 1987

Production of layer-type magnetic recording media

INVENTOR: Lehner, August, Roedersheim-Gronau, Federal Republic of Germany  
Balz, Werner, Limburgerhof, Federal Republic of Germany  
Lenz, Werner, Bad Dürkheim, Federal Republic of Germany

Kohl, Albert, Laumersheim, Federal Republic of Germany  
Heil, Guenter, Ludwigshafen, Federal Republic of Germany

We claim:

[\*1] 1. A process for the production of a layer-type magnetic recording medium by dispersing a finely divided magnetically anisotropic material in a binder which consists of not less than 40% of a radiation-curable aqueous binder dispersion, applying the ...

LEVEL 1 - 114 OF 225 PATENTS

4,671,235

<=2> GET 1st DRAWING SHEET OF 2

Jun. 9, 1987

Tissue expander with self-contained injection reservoir and reinforcing insert

INVENTOR: Dubrul, William R., Santa Barbara, California  
Heyler, III, Charles J., Thousand Oaks, California

... [\*11] claim 10 wherein the plastic resin embedding the magnetically detectable material is further embedded in a silicone elastomer.

[\*12] 12. A tissue expander device for surgical implantation beneath the skin and the subcutaneous layer of the type which is expanded after implantation by periodic injection of a liquid, such as saline into the expander device, the tissue expander comprising:

a thin expandable biocompatible cast silicone elastomer envelope forming an expandable ...

... [\*16] tissue expander of claim 15 wherein the magnet in the injection reservoir is embedded in vapor barrier material.

[\*17] 17. In a tissue expander used for surgical implantation beneath the skin and the subcutaneous layer of the type which is expanded after implantation by periodic injection of liquid into the expander device, the tissue expander having an expandable biocompatible envelope forming an expandable fluid-tight chamber configured to include an apex and an injection reservoir fully ...

... [\*22] reservoir whereby location of the injection reservoir can be ascertained by external means for locating the magnet.

[\*23] 23. In a tissue expander used for surgical implantation beneath the skin and the subcutaneous layer of the type which is expanded after implantation by periodic injection of a liquid into the expander device, the tissue expander having an expandable biocompatible envelope forming an expandable fluid-tight chamber configured to include an apex and an injection reservoir ...

LEVEL 1 - 115 OF 225 PATENTS

4,667,209

<=2> GET 1st DRAWING SHEET OF 3

May 19, 1987

Image recording apparatus

INVENTOR: Hakamada, Isao, Yokohama, Japan  
Matsuoka, Kazuhiko, Yokohama, Japan

We claim:

[\*1] 1. An image recording apparatus comprising:

a multi-layer type photosensitive medium; and

means for recording images by scanning said photosensitive medium with a laser beam, said means including a semiconductor laser which produces multimode oscillations, said laser ...

LEVEL 1 - 116 OF 225 PATENTS

4,664,857

May 12, 1987

Process for preparing a hydrogel

INVENTOR: Nambu, Masao, Yokohama, Japan

... [\*1] a water-insoluble hydrogel having a water content of 20 to 92% by weight.

[\*2] 2. A process according to claim 1, in which clay minerals of a laminated structure having a three-layer type (2:1 type) composite layer as a basic unit are suspended in said aqueous polyvinyl alcohol solution in an amount of not more than five times by weight the amount of said ...

LEVEL 1 - 117 OF 225 PATENTS

4,664,843

May 12, 1987

Mixed metal layered hydroxide-clay adducts as thickeners for water and other hydrophylic fluids



INVENTOR: Burba, III, John L., Angerton, Texas  
Barnes, Audrey L., Lake Jackson, Texas

... [\*16] vermiculite, chlorite, attapulgite, sepiolite, palygorskite, and Fuller's earth.

[\*17] 17. The composition of claim 1 wherein [tne] the mineral clay is at least one of the classes consisting of amorphous clays of the allophane group and crystalline clays of the 2-layer type, 3-layer type, expanding type, non-expanding type, elongate type, regular mixed layer type, and chain structure type.

[\*18] 18. The composition of claim 1 wherein the mineral clay is bentonite.

[\*19] 19. The composition of claim 1 wherein the mineral clay is beneficiated bentonite.

[\*20] 20. The composition of claim 1 wherein the weight ratio of layered  
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... LEVEL 1 - 118 OF 225 PATENTS

4,659,401

<=2> GET 1st DRAWING SHEET OF 2

Apr. 21, 1987

Growth of epitaxial films by plasma enhanced chemical vapor deposition (PE-CVD)

INVENTOR: Reif, L. Rafael, Newton, Massachusetts  
Fonstad, Jr., Clifton G., Arlington, Massachusetts

... [\*11] establishing a steady state flow of said first set of gaseous reactants in said chamber, said reactants having a concentration of atoms of a first type conductivity, such as to produce a layer of that type conductivity when deposited;

(c) after steady state flow is achieved heating said substrate to a temperature high enough to obtain epitaxial deposition from the first set of reactants when a decomposition reaction occurs ...  
LEVEL 1 - 119 OF 225 PATENTS

4,644,335

<=2> GET 1st DRAWING SHEET OF 4

Feb. 17, 1987

Apparatus and method for monitoring drill bit condition and depth of drilling

INVENTOR: Wen, Sheree H., Mohegan Lake, New York

... [\*1] number of occurrences of the waveform representing the acoustic signature for each type of layer; and

means for stopping the drilling operation upon reaching a predetermined count of waveform occurrences for a particular layer type.

[\*2] 2. The apparatus of claim 1 wherein said control means includes a computer for comparing the detected sequence of waveforms to a reference sequence of waveforms stored in said computer corresponding to the multilayered ...

... [\*6] type of layer for each signal; and

means for separately stopping the drilling operation of at least one drill bit upon reaching a predetermined count of waveform occurrences for a particular layer type for each drill bit.

[\*7] 7. The apparatus of claim 1 or 6 further including a filter means for filtering out low and high frequency noise.

[\*8] 8. In a multiple ...

... [\*8] said reference signal representing an acoustic signature for a proper drill bit drilling having each type of layer, for counting the number of occurrences of the waveform representing the acoustic signature for each layer type for each of said drill bits, and for detecting when the acoustic signature of at least one of said output signals is different from the acoustic signature of said reference signal thereby detecting an improper drill bit condition; and

...

... [\*8] bit upon detection of an improper drill bit condition; and

means for stopping the drilling operation of at least one drill bit upon reaching a predetermined count of waveforms occurrences of a particular layer type for one or more drill bits.

[\*9] 9. A method for drilling to a predetermined depth of a multilayer workpiece comprising:

acoustically detecting drill bit vibrations as the drill bit ...

... [\*9] layer;

Pat. No. 4644335, \*9

counting the number of occurrences of the waveform representing the acoustic signatures for each type of layer; and

stopping the drilling operation upon reaching a predetermined count of waveform occurrences for a particular layer type.

[\*10] 10. The method of claim 9 further including the steps of producing an output signal having a sequence of waveforms representing the acoustic signatures corresponding to the sequence of layers, comparing the sequence of waveforms to a reference sequence and ...

... [\*12] least one of said output signals and said reference signal; and stopping the drilling operation of at least one drill bit upon reaching a predetermined count of waveform occurrences for a particular layer type for one or more drill bits.

PAGE 132

LEVEL 1 - 120 OF 225 PATENTS

4,629,632

Dec. 16, 1986

Production of magnetic recording media

INVENTOR: Balz, Werner, Limburgerhof, Federal Republic of Germany  
Kovacs, Jenoe, Hesseheim, Federal Republic of Germany  
Lechner, Hilmar, Frankenthal, Federal Republic of Germany  
Schaefer, Dieter, Lindenberg, Federal Republic of Germany  
Buethe, Ingolf, Boehl-Iggelheim, Federal Republic of Germany

We claim:

[\*1] 1. A process for the production of a layer-type magnetic recording medium by applying a dispersion of a magnetically anisotropic material in a binder solution onto a flexible plastic base provided with an adhesion-promoting intermediate layer and then solidifying the ...

LEVEL 1 - 121 OF 225 PATENTS

4,617,423

<=2> GET 1st DRAWING SHEET OF 6

Oct. 14, 1986

Data communication system

INVENTOR: Dickerson, James W., Plano, Texas  
Smith, III, William N., Carrollton, Texas

What is claimed is:

[\*1] 1. A network multiple physical layer interface connected to a communications network of a first physical layer type and a second physical layer type, each layer type including a send channel and a receive channel, said interface comprising:

PAGE 133

a first circuit means for receiving data from said first physical layer send channel and receive channel and ...

LEVEL 1 - 122 OF 225 PATENTS

4,614,185

<=2> GET 1st DRAWING SHEET OF 1

Sep. 30, 1986

Piston engine having a phosphatized cylinder wall

INVENTOR: Fox, Richard C., Mobile, Alabama

... [\*4] 1, wherein said integral layer of crystalline phosphate is characterized by resistance to wear by said piston ring during operation of said engine.

[\*5] 5. The invention according to claim 1, wherein said integral layer is of the type assisting the seating of said piston ring in said cylinder.

[\*6] 6. The invention according to claim 1, wherein said cylinder head is an aluminum cylinder head.

[\*7] 7. The invention according to claim 6, wherein said ...  
GE 135

LEVEL 1 - 123 OF 225 PATENTS

4,611,114

<=2> GET 1st DRAWING SHEET OF 2

Sep. 9, 1986

Photoelectric detection structure having substrate with controlled properties

INVENTOR: Dolizy, Pierre, Ris-Orangis, France  
Groliere, Francoise, Nogent-sur-Marne, France  
Maniguet, Francois, Fontenay-Tresigny, France

... [\*8] according to claim 7, wherein said tri-alkaline material is SbNa2K, Cs.

[\*9] 9. A photoelectric detection structure according to claim 7, wherein said photosensitive layer has a thickness corresponding to a photoelectric layer of the type S20 or S25.

[\*10] 10. A photoelectric detection structure according to claim 2, wherein said photosensitive layer is a bi-alkaline photosensitive material.

[\*11] 11. A photoelectric detection structure according to claim ...  
PAGE 136

LEVEL 1 - 124 OF 225 PATENTS

4,604,673

Aug. 5, 1986

Distribution transformer with surge protection device

INVENTOR: Schoendube, Charles W., Hickory, North Carolina

What I claim as new is:

[\*1] 1. A distribution-type single-phase transformer having a surge protection arrangement comprising:

(a) a layer-type high voltage winding having two terminals, one being a high voltage terminal for connection to a high voltage line,

(b) a divided low voltage winding comprising two ...  
LEVEL 1 - 125 OF 225 PATENTS

4,587,720

<=> GET 1st DRAWING SHEET OF 1

May 13, 1986

Process for the manufacture of a self-aligned thin-film transistor

INVENTOR: Chenevas-Paule, Andre , Grenoble, France  
Diem, Bernard, Meylan, France

... [\*2] wavelength of the order of 600 nanometers.

[\*3] 3. A process according to claim 1, wherein step (h) comprises:  
depositing a layer of n + type amorphous silicon on the entire structure;

depositing a conducting layer on the type n + silicon layer;

eliminating the regions respectively of the conducting layer and of the type n + silicon layer situated in line with said grid; and

making the electrodes of the source and of the drain in said conducting layer.

[\*4] 4. A process according to claim 1, wherein said insulating layer is ...  
PAGE 138

LEVEL 1 - 126 OF 225 PATENTS

4,584,553

Apr. 22, 1986

Coated layer type resistor device

INVENTOR: Tokura, Norihito, Nukata, Japan  
Kawai, Hisasi, Toyohashi, Japan

We claim:

[\*1] 1. A coated layer type resistor device comprising:

an insulator substrate;

a first resistor element formed on said insulator substrate and consisting of a resistor layer and end conductor electrodes at the ends of said resistor layer; and

a ...

... [\*1] conductor electrodes and the adjacent intermediate conductor in said second resistor element being equal to the distance between end conductor electrodes in said first resistor element.

[\*2] 2. A coated layer type resistor device according to claim 1, wherein: said end conductor electrodes and said intermediate conductors are formed by printing on said insulator substrate;

on said insulator substrate having said formed end conductor electrodes and intermediate conductors, a resistor layer is formed by printing; and

said formed resistor layer is in contact with said formed end conductor electrodes and intermediate conductors.

[\*3] 3. A coated layer type resistor device according to claim 1, wherein a bridge circuit is constituted by said first and second resistor elements.

PAGE 139

LEVEL 1 - 127 OF 225 PATENTS

4,576,116

<=2> GET 1st DRAWING SHEET OF 1

Mar. 18, 1986

Collapsible house for cats

INVENTOR: Binkert, Gerald A., 308 Gould Ave. SE., Bemidji, Minnesota 56601

... [\*1] A collapsible A-frame house providing a common site for a cat to rest, exercise and play, comprising

(a) a roof formed of a single unitary continuous flexible layer-type material having a backside and a cushiony outward face, said roof including an elongate peak and two roof panels integral with the peak and depending downwardly and outwardly from the peak, each said roof panel having a bottom edge, the outward face of the flexible layer-type material being the outward face of the roof and being adapted to withstand cat clawing, the peak of the roof being adapted for flexing in a hinge-like manner to permit inward movement of the roof ...

... [\*1] another when the house is to be collapsed;

(b) a stiffening means on the backside of each roof panel for supporting the same;

(c) a floor panel formed of a single unitary continuous flexible layer-type material having a bottom side and a cushiony top side, said floor panel having opposing edges thereof affixed to the bottom edges of the roof panels to limit the separation distance between said bottom edges, the floor panel being adapted for folding along its longitudinal center line generally parallel to its opposing edges, and the flexible layer-type material adjacent the junction of the bottom edges of the roof panels and the opposing edges of the floor panel being such as to serve a hinge function for allowing the floor panel to fold as the roof panels ...

... [\*10] A collapsible A-frame house providing a common site for a cat to rest, exercise and play, comprising

(a) a roof formed of a single unitary continuous flexible layer-type material having a backside and a cushiony outward face, said roof including an elongate peak and two roof panels integral with the peak and depending downwardly and outwardly from the peak, each said roof panel having a bottom edge, the outward face of the flexible layer-type material being the outward face of the roof and being adapted to withstand cat clawing, the peak of the roof being adapted for flexing in a hinge-like manner to permit inward movement of the roof ...

... [\*10] another when the house is to be collapsed;

(b) a stiffening means on the backside of each roof panel for supporting the same; and

(c) a floor panel formed of a single unitary continuous flexible layer-type material having a bottom side and a cushiony top side, said floor panel having opposing edges thereof affixed by staples to the bottom edges of the roof

PAGE 140

Pat. No. 4576116, \*10

panels to limit the separation distance between said bottom edges, the floor panel being adapted for folding along its longitudinal center line generally parallel to its opposing edges, and the flexible layer-type material adjacent the junction of the bottom edges of the roof panels and the opposing edges of

the floor panel being such as to serve a hinge function for allowing the floor panel to fold as the roof panels ...

PAGE 141

LEVEL 1 - 128 OF 225 PATENTS

4,566,460

<=2> GET 1st DRAWING SHEET OF 13

Jan. 28, 1986

Measuring method and apparatus for non-linear parameter of acoustic medium and its application

INVENTOR: Sato, Takuso, Tokyo, Japan  
Ichida, Nobuyuki, Machida, Japan  
Miwa, Hirohide, Kawasaki, Japan

... [\*20] reception characteristics sufficient to cover both receiving said probing wave and transmitting said pumping wave.

[\*21] 21. An apparatus according to claim 10, wherein said second and said third transducer comprise a layer type transducer, having a front layer as said second transducer, and a back layer as said third transducer.

[\*22] 22. An apparatus according to claim 6, wherein said third means comprises:

phase ...

LEVEL 1 - 129 OF 225 PATENTS

4,560,419

PAGE 142

<=2> GET 1st DRAWING SHEET OF 3

Dec. 24, 1985

Method of making polysilicon resistors with a low thermal activation energy

INVENTOR: Bourassa, Ronald R., Colorado Springs, Colorado  
Butler, Douglas B., Colorado Springs, Colorado

... [\*11] 11. The method of claim 7 including establishing said first, second and third poly regions to form back-to-back polysilicon diodes.

[\*12] 12. The method of claim 8 including doping a poly layer with the type of impurity for said first region of poly, then defining the poly which is to act as the resistor, the selectively doping said second and third regions of poly with the other type of impurity.

[\*13] 13. The method of claim 12 wherein the ...  
LEVEL 1 - 130 OF 225 PATENTS

PAGE 143



4,547,784

<=2> GET 1st DRAWING SHEET OF 6

Oct. 15, 1985

Thermal recording system and method

INVENTOR: Erlichman, Irving, Wayland, Massachusetts  
Haussein, Robert W., Lexington, Massachusetts

... [\*1] for recording an image represented by pixel areas of varied density on a transparency type thermally sensitive recording medium having a transparent support layer and a transparent thermally sensitive recording layer of the type wherein recorded dot size increases with increased amounts of thermal energy applied to form a dot, said recording system comprising:

means for supporting such a transparency type of recording medium;

means ...

LEVEL 1 - 131 OF 225 PATENTS

4,525,223

<=2> GET 1st DRAWING SHEET OF 16

Jun. 25, 1985

Method of manufacturing a thin ribbon wafer of semiconductor material

INVENTOR: Tsuya, Noboru, 1-38, Kashiwagi 2-Chome, Sendai, Japan  
Arai, Kenichi, Sendai, Japan

... [\*18] moving direction of the cooling substrate and at least two jet flows of semiconductor and gaseous or molten material including the same semiconductor are simultaneously ejected through the holes so as to form a thin ribbon of multiple-layer type.

[\*19] 19. A method as defined in claim 1, wherein the thin ribbon is heat-treated at a temperature within the range from 500o C. to a melting point for a time of 0.1 ...

LEVEL 1 - 132 OF 225 PATENTS

4,523,906

<=2> GET 1st DRAWING SHEET OF 8

Jun. 18, 1985

Device for drying gypsum

PAGE 144

PAGE 145

INVENTOR: Petrovic, Vladan, Essen, Federal Republic of Germany

... [\*1] cold, wet gypsum, comprising a heater; means for feeding a plurality of heat-retaining solid particles into said heater; means for storing gypsum to be dried; a moving-layer-type drier in the form of an upright stationary container having an inlet at its top, an outlet at its bottom and a plurality of superposed funnel-like means arranged between the inlet and the outlet; means for conveying an amount of hot ...

... [\*6] cold, wet gypsum, comprising a heater; means for feeding a plurality of heat-retaining solid particles into said heater; means for storing gypsum to be dried; a moving-layer-type drier in the form of an upright stationary container having an inlet at its top, an outlet at its bottom and a plurality of superposed funnel-like means arranged between the inlet and outlet; means for intermixing the amount of hot ...

LEVEL 1 - 133 OF 225 PATENTS

4,513,016

Apr. 23, 1985

No-stir dry mix with pudding nuggets for cake with  
discontinuous pudding phase

INVENTOR: Blake, Jon R., 6901 Regent Ave N., Brooklyn Center, Minnesota 55429  
Knutson, Richard K., 6948 Valley View Rd., Corcoran, Minnesota 55340  
VanHulle, Glenn J., 7608 Major Ave. N., Brooklyn Park, Minnesota 55443

... [\*14] length.

[\*15] 15. The dry mix of claim 14 wherein the weight ratio of sugar to granules in the matrix ranges from about 1:5 to 1:6.

[\*16] 16. A method for preparing a finished cake of a layer type having after baking a discontinuous pudding phase, in the finished baked cake consisting essentially of the steps of:

A. providing a dry mix for cakes, said dry mix comprising

I. from ...

LEVEL 1 - 134 OF 225 PATENTS

4,510,443

<=2> GET 1st DRAWING SHEET OF 4

Apr. 9, 1985

Voltage measuring device

INVENTOR: Inaba, Ritsuo, Hirakata, Japan  
Wasa, Kiyotaka, Nara, Japan

What is claimed is:

[\*1] 1. A voltage measuring device for receiving and measuring a voltage to be measured and for providing an output signal corresponding thereto, said device comprising:

a first medium of the double layer type for propagating surface acoustic waves, said first medium comprising a piezoelectric thin film which is laminated on a substrate comprising a non-piezoelectric material;

a first transducer means ...

PAGE 148

LEVEL 1 - 135 OF 225 PATENTS

4,506,004

<=2> GET 1st DRAWING SHEET OF 3

Mar. 19, 1985

Printed wiring board

INVENTOR: Sullivan, Donald F., 115 Cambridge Rd., King of Prussia, Pennsylvania 19406

... [\*5] substrate, and

developing the photo images by washing out the unhardened photopolymer, whereby removal of the unhardened liquid polymer layer in contact with the substrate is simple and complete.

[\*6] 6. The process of claim 5 wherein the laminated photopolymer layers are of the type that are hardened by exposure to the radiation.

[\*7] 7. The photo process of claim 6 including the step of partly curing the liquid photopolymer second layer by exposure to radiation before lamination.

[\*8] 8. The photo process of ...

LEVEL 1 - 136 OF 225 PATENTS

4,501,303

<=2> GET 1st DRAWING SHEET OF 2

Feb. 26, 1985

Forming fabric

PAGE 149

INVENTOR: Osterberg, Lars B., Halmstad, Sweden

What I claim is:

[\*1] 1. An improved double-layer type of forming fabric for use in papermaking, cellulose and similar machines, said forming fabric consisting of two integral weaves, each one of said weaves comprising its separate sets of respective warp ...

PAGE 150

LEVEL 1 - 137 OF 225 PATENTS

4,494,826

<=2> GET 1st DRAWING SHEET OF 2

Jan. 22, 1985

Surface deformation image device

INVENTOR: Smith, James L., 426 High School Dr., Grand Prairie, Texas 75050

... [\*2] set forth in claim 1 wherein said grille structure layer is inside said photoconductive layer.

[\*3] 3. A device as set forth in claim 1 or 2 wherein said photoconductor

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Received: from igw2.watson.ibm.com (igw2.watson.ibm.com [9.2.250.12]) by mailhub.watson.ibm.com (8.8.7/Feb-20-98) with ESMTP id MAA12876 f or <dmorris@watson.ibm.com>; Tue, 22 Dec 1998 12:45:19 -0500  
Received: from prod.lexis-nexis.com (prod.lexis-nexis.com [138.12.4.30]) by igw2.watson.ibm.com (8.8.7/07-11-97) with SMTP id MAA64762 for <dmorris@watson.ibm.com>; Tue, 22 Dec 1998 12:45:16 -0500  
Received: by prod.lexis-nexis.com id AA26469  
(InterLock SMTP Gateway 3.0 for dmorris@watson.ibm.com);  
Tue, 22 Dec 1998 12:45:15 -0500  
Message-Id: <199812221745.AA26469@prod.lexis-nexis.com>  
Received: by prod.lexis-nexis.com (Internal Mail Agent-1);  
Tue, 22 Dec 1998 12:45:15 -0500  
Date: Tue, 22 Dec 1998 12:45:14 -0500  
From: lexis-nexis@prod.lexis-nexis.com (LEXIS(R)/NEXIS(R) Print Delivery)  
To: dmorris@watson.ibm.com  
Subject: LEXIS(R)/NEXIS(R) Print Request Job 68990, 3 of 4

layer is of the type which requires high electric field for significant photoconduction such as CdS powder in plastic.

[\*4] 4. A device as set forth in claim 1 wherein a nonconducting light blocking ...

PAGE 151

LEVEL 1 - 138 OF 225 PATENTS

4,477,547

Oct. 16, 1984

Method for making complex layer type lithographic printing plate

INVENTOR: Yamada, Jun, Nagaokayo, Japan  
Senga, Takao, Nagaokayo, Japan  
Suzuki, Shigeoyoshi, Nagaokayo, Japan

What is claimed is:

[\*1] 1. A method for making a complex layer type lithographic printing plate which comprises forming a toner image on an original printing plate having organic electrophotographic photosensitive layer by electrophotographic process, said photosensitive layer being a complex layer type photosensitive layer which comprises a charge carrier generating layer comprising a charge carrier generating substance and a binder mainly composed of a polyamide resin soluble in alcohol solvent and ...

... [\*1] solution mainly composed of alcohol solvent and/or alkali solvent and thereafter treating non-image area other than the toner image area with the etching solution.

[\*2] 2. A method for making a complex layer type lithographic printing plate according to claim 1, wherein the polyamide resin of the binder for the charge carrier generating layer is copolymer nylon.

[\*3] 3. A method for making a complex layer type lithographic printing plate according to claim 1 wherein the high molecular substance of the binder for the charge carrier generating layer is one having acid anhydride group, carboxylic acid group, sulfonic acid group or sulfonimide group.

[\*4] 4. A method for making a complex layer type lithographic printing plate according to claim 1 wherein the charge carrier generating substance is an organic pigment or sensitizing dye.

[\*5] 5. A method for making a complex layer type lithographic printing plate according to claim 1 wherein the charge carrier transport substance is an aromatic tertiary amino compound, an aromatic tertiary diamino compound, an aromatic tertiary triamino compound, a condensate or a heterocyclic compound.

[\*6] 6. A method for making a complex layer type lithographic printing plate according to claim 1 wherein the high molecular substance contained in the binder for the charge carrier transfer layer is one having acid anhydride group, carboxylic acid group, sulfonic acid group or sulfonimide group or a phenolic resin.

[\*7] 7. An original printing plate having organic electrophotographic photosensitive layer on a support for complex layer type lithographic printing plate on which a toner image is formed, said photosensitive layer comprising a charge carrier generating layer comprising a charge carrier generating substance and a binder mainly ...

Pat. No. 4477547, \*7

... [\*7] a high molecular substance having a group soluble in an etching solution mainly composed of alcohol solvent and/or alkali solvent.

[\*8] 8. A printing method which comprises carrying out printing with the complex layer type lithographic printing plate made by the method of claim 1.

PAGE 153

LEVEL 1 - 139 OF 225 PATENTS

4,470,024

<=2> GET 1st DRAWING SHEET OF 2

Sep. 4, 1984

Integrated circuit for a controllable frequency oscillator

INVENTOR: Leuenberger, Claude-Eric, Chezard, Switzerland

... [\*1] said insulating layer, said chip having an oxide layer, said insulating layer being a portion of said oxide layer.

[\*2] 2. The chip of claim 1, wherein said first region is a bulk layer of the type of conductivity opposite to said one type of conductivity, said bulk layer being formed in said semiconductor substrate, and said second region is a

diffusion portion of said one type of conductivity ...  
LEVEL 1 - 140 OF 225 PATENTS

PAGE 154

4,451,843

<=2> GET 1st DRAWING SHEET OF 2

May 29, 1984

Bipolar transistor with a plurality of parallelly connected  
base-collector junctions formed by plastic deformation of  
the crystal lattice

INVENTOR: Dahlberg, Reinhard, Flein, Federal Republic of Germany

... [\*1] emitter region on its opposite main face so as to form an  
emitter-base p/n junction; the side surfaces of the ridges in the other  
semiconductor plate, disc or chip have a highly doped surface layer with the  
type of conductivity of the base region; both semiconductor discs are assembled,  
by mechanical pressure, so that the ridges of the structured faces of both  
plates, discs or chips cross and touch; and the surfaces of said ridges which  
are in contact are connected ...

LEVEL 1 - 141 OF 225 PATENTS

PAGE 155

4,427,607

<=2> GET 1st DRAWING SHEET OF 6

Jan. 24, 1984

Device in an evaporative cooler

INVENTOR: Korsell, Lars E. R., Stockholm, Sweden

... [\*4] telescopically received only in the corresponding top openings of  
a similar contact body immediately therebelow.

[\*5] 5. In an evaporative cooler including, a casing, at least one contact  
body of the multi-layer type located in said casing and formed with channels  
existing between the layers and which all are passed by air, and means for  
supplying water to selected channels in said body from above the body, the  
improvement comprising ...

LEVEL 1 - 142 OF 225 PATENTS

PAGE 156

4,422,627

<=2> GET 1st DRAWING SHEET OF 1

Dec. 27, 1983

Endless spring, such as ringspring

INVENTOR: Schmidt, Helmut, Munich, Neubiberg, Federal Republic of Germany  
Ramm, Ulrich, Neubiberg, Federal Republic of Germany  
Schroeder, Alexander, Ottobrunn, Federal Republic of Germany

... [\*1] comprising a spring body having a plurality of layers (2, 3, 4) made of fiber compound materials and extending in parallel to said frame plane, said layers comprising a first layer type (2) in which fiber bundles are wound so that all the fibers extend unidirectionally in said first layer type and a second layer type (3, 4), each said second layer type comprising at least two plies (5, 6) in which the fibers extend in cross-over relationship relative to each other, said first layer type and said second layer type being arranged in alternate succession relative to each other.

[\*2] 2. The endless spring of claim 1, wherein said second layer type comprises one layer more than said first layer type so that the second layer type forms outer surfaces parallel to said frame plane, and so that said first layer type forms inner layers interconnected by a second type layer between two neighboring first type layers.

[\*3] 3. The endless spring of claim 1, wherein said plies (5, 6) of said second layer type (3, 4) comprise at least one first ply (5) with fibers extending in parallel and at 90° relative to said main load application direction, and at least one second ply (6) with fibers extending in a +/- 45° cross-over relationship relative to said main load application direction.

[\*4] 4. The endless spring of claim 3, wherein each of said second layer type (3, 4) comprises said first and second plies (5, 6), wherein a second layer type (3) located internally of the spring between two first layer types (2) comprises at least two first plies (5) and a second ply (6) located between said two first plies (5), and wherein a second layer type (4) located externally of the spring comprises at least one first ply (5) and at least one second ply (6) located on the outside of the spring.

[\*5] 5. The spring of claim 1, wherein each of said first layer type (2) comprises at least two fiber bundles.

[\*6] 6. The spring of claim 1, wherein said plies of said second layer type are made of fibers of different materials.

[\*7] 7. The spring of claim 1, wherein said fiber bundles of said first layer type (2) are made of fibers of different materials.

[\*8] 8. The spring of claim 1, wherein said fiber bundles of said first layer type (2) and said plies of said second layer type (3, 4) are made of fibers of different materials.

Pat. No. 4422627, \*8

[\*9] 9. The spring of claim 1, further comprising adhesive layers (7) operatively interposed between said first and second layer types.



[\*10] 10. The spring of claim 1, further comprising spring attachment means (8) operatively secured to said endless spring for applying a load to the spring, and wear resistant plate means (9) ...

... [\*10] reducing the wear imposed by the attachment means on the spring.

[\*11] 11. The spring of claim 10, wherein said plate means (9) are made of spring steel.

[\*12] 12. The spring of claim 1, wherein said first and second layer types (2, 3, 4) form an endless loop having two straight legs extending in parallel to each other and two curved end portions operatively interconnecting said straight legs.

[\*13] 13. The spring of ...  
LEVEL 1 - 143 OF 225 PATENTS

4,419,310

<=2> GET 1st DRAWING SHEET OF 2

Dec. 6, 1983

SrTiO3 barrier layer capacitor

INVENTOR: Burn, Ian, Williamstown, Massachusetts  
Neirman, Stephen M., Williamstown, Massachusetts

What is claimed is:

[\*1] 1. A method for making an intergranular barrier layer type capacitor without heating in a reduced atmosphere comprising:

(a) preparing a ceramic start mixture consisting essentially of strontium, titanium and strontium-titanate donor compounds, said donors being ...

PAGE 159

LEVEL 1 - 144 OF 225 PATENTS

4,414,059

<=2> GET 1st DRAWING SHEET OF 3

Nov. 8, 1983

Far UV patterning of resist materials

INVENTOR: Blum, Samuel E., White Plains, New York  
Brown, Karen H., Yorktown Heights, New York  
Srinivasan, Rangaswamy, Ossining, New York

... [\*7] final step thereof includes the treatment of said exposed portions of said substrate through said patterned resist layer to modify the characteristics of said exposed portions.

[\*8] 8. A method for patterning resist layers of the type used in lithography processes, comprising the steps of:

depositing a layer of said resist on a substrate, and

irradiating selected areas of said resist layer with ultraviolet radiation having wavelengths less than 220 nm and an ...

LEVEL 1 - 145 OF 225 PATENTS

PAGE 160

4,411,539

<=2> GET 1st DRAWING SHEET OF 7

Oct. 25, 1983

Print element with plural type layers of varying thickness

INVENTOR: Iwata, Nobuo, Sagamihara, Japan;  
Hasegawa, Takashi, Hiratsuka, Japan

... [\*1] by the hammer, and the vertical dimension of the character carried by the type member; such variance in thicknesses eliminating ghost printing caused by the undesired touching of the paper by the type member adjacent in layer to the type member struck by the member.

[\*2] 2. A print element as claimed in claim 1, wherein the print element is formed in a form of a disc type print wheel including ...  
LEVEL 1 - 146 OF 225 PATENTS

PAGE 161

4,405,533

<=2> GET 1st DRAWING SHEET OF 4

Sep. 20, 1983

Supply device for use with evaporative contact bodies

INVENTOR: Norback, Per, Lidingo, Sweden  
Eriksson, Borje, Sigtuna, Sweden

We claim:

[\*1] 1. A supply device for use in a evaporative contact body of the multi-layer type having gaps between the layers of the body to which water is supplied from above and air is supplied from below, said device comprising water supply pipes and means for forming jets of water and directing said water jets ...

PAGE 162

LEVEL 1 - 147 OF 225 PATENTS

4,403,236

Sep. 6, 1983

Boundary layer type semiconducting ceramic capacitors with high capacitance

INVENTOR: Mandai, Haruhumi, Nagaokakyo, Japan  
Nishimura, Kunitaro, Youkaichi, Japan  
Yamaguchi, Masami, Nagaokakyo, Japan

What we claim is:

[\*1] 1. A boundary layer type semiconducting ceramic capacitor comprising a semiconducting ceramic body in which grain boundaries on crystal grains of the semiconducting ceramic body are insulated, characterized in that said semiconducting ceramic body has a composition ...

... [\*1] consisting of Mn, Bi, Cu, Pb, B and Si, and that the maximum crystal grain present in the semiconducting ceramic body has a grain size ranging from 100 mu to 250 mu .

[\*2] 2. The boundary layer type semiconducting ceramic capacitor according to claim 1 wherein said composition contains 0.02 to 0.2 mole % of Mn.

[\*3] 3. The boundary layer type semiconducting ceramic capacitor according to claim 2 wherein Mn is present in at least one of the grain boundaries and the crystal grains.

[\*4] 4. The boundary layer type semiconducting ceramic capacitor according to claim 1 wherein said composition further contains at least one of 0.05 to 0.5 mole % of SiO<sub>2</sub> and 0.02 to 0.2 mole % of Al<sub>2</sub>O<sub>3</sub>.

[\*5] 5. The boundary layer type semiconducting ceramic capacitor according to claim 2 wherein said composition further contains at least one of 0.05 to 0.5 mole % of SiO<sub>2</sub> and 0.02 to 0.2 mole % of Al<sub>2</sub>O<sub>3</sub>.

[\*6] 6. The boundary layer type semiconducting ceramic capacitor according to claim 2 wherein Mn is present in the crystal grains.

[\*7] 7. The boundary layer type semiconducting ceramic capacitor according to claim 2 wherein Mn is present in the grain boundaries of the crystal grains, and wherein said grain boundaries of the crystal grains are insulated by Mn and at least one other insulating agent.

[\*8] 8. The boundary layer type semiconducting ceramic capacitor according to claim 1 in which the amount of the main component is 98.1 to 99.88 mole %.

[\*9] 9. The boundary layer type semiconducting ceramic capacitor according to claim 8 wherein Mn is present at at least one of the grain boundaries and the crystal grains.

[\*10] 10. The boundary layer type semiconducting ceramic capacitor according to claim 9 wherein Mn is present at the crystal grains.  
GE 163

Pat. No. 4403236, \*10

[\*11] 11. The boundary layer type semiconducting ceramic capacitor according to claim 10 wherein said composition further includes at least one of 0.05 to 0.5 mole % of SiO<sub>2</sub> and 0.02 to 0.2 mole % of Al<sub>2</sub>O<sub>3</sub>.

[\*12] 12. The boundary layer type semiconducting ceramic capacitor according to claim 9 wherein said composition further includes at least one of 0.05 to 0.5 mole % of SiO<sub>2</sub> and 0.02 to 0.2 mole % of Al<sub>2</sub>O<sub>3</sub>.

[\*13] 13. The boundary layer type semiconducting ceramic capacitor according to claim 8 wherein said main component is (Sr<sub>1</sub> - xBa[x])TiO<sub>3</sub>.

[\*14] 14. The boundary layer type semiconducting ceramic capacitor according to claim 1 wherein said main component is (Sr<sub>1</sub> - xBa[x])TiO<sub>3</sub>.  
PAGE 164

LEVEL 1 - 148 OF 225 PATENTS

4,397,886

<=2> GET 1st DRAWING SHEET OF 1

Aug. 9, 1983

Method for making a ceramic intergranular barrier-layer capacitor

INVENTOR: Neirman, Stephen M., Williamstown, Massachusetts  
Burn, Ian, Williamstown, Massachusetts

What is claimed is:

[\*1] 1. A method for making a ceramic intergranular barrier layer type capacitor comprising:

(a) preparing a ceramic start mixture consisting essentially of strontium, titanium, a strontium-titanate-donor and manganese, said donor being selected from large cations A, small ...

LEVEL 1 - 149 OF 225 PATENTS

4,386,135

May 31, 1983

Stable silicone-coated release liner for pressure-sensitive adhesive sheets

INVENTOR: Campbell, Karen J., Anoka, Minnesota  
Evans, Jack L., St. Paul, Minnesota

... [\*1] hydrogen in (2) to silicon-bonded ethylenically unsaturated radicals in (1) being from 1:1 to 20:1.

[\*2] 2. The release liner of claim 1 wherein each side of the base sheet is provided with a silicone layer of the type defined.

[\*3] 3. The release liner of claim 1 wherein R and R<1 > are both methyl.

[\*4] 4. The release liner of claim 1 wherein R<2 > is a vinyl radical.

[\*5] 5. The release liner of claim ...  
LEVEL 1 - 150 OF 225 PATENTS

4,363,997

<=2> GET 1st DRAWING SHEET OF 2

Dec. 14, 1982

Fluorescent lamp having reflective layer

INVENTOR: Kodama, Churyo, Ohme, Japan

What is claimed is:

[\*1] 1. A fluorescent lamp of the reflective layer type comprising a glass tube, a first phosphor layer formed on the entire face of the inner wall of said glass tube and a second phosphor layer formed on said first phosphor layer at ...

... [\*1] m and the average particle size of the phosphor constituting said first phosphor layer is smaller than the average particle size of the phosphor constituting said second phosphor layer.

[\*2] 2. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the average particle size of the phosphor constituting the first phosphor layer is smaller than 10  $\mu$  m.

[\*3] 3. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the average particle size of the phosphor constituting the second phosphor layer is smaller than 30  $\mu$  m.

[\*4] 4. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein each of the amounts coated of the phosphors of the first and second phosphor layers is 2 to 4 mg/cm<2>.

[\*5] 5. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the reflection angle is in the range of 180 to 240°.

[\*6] 6. A fluorescent lamp of the reflective layer type as set forth in claim 5, wherein the reflection angle is 180°.

[\*7] 7. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the phosphor constituting the first phosphor layer has the same light emission spectrum as that of the phosphor constituting the second phosphor layer.

[\*8] 8. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the phosphor constituting the first phosphor layer has a light emission spectrum different from that of the phosphor constituting the second phosphor layer.

[\*9] 9. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the glass tube is a straight tube.

[\*10] 10. A fluorescent lamp of the reflective layer type as set forth in claim 1, wherein the glass tube is a circular or curved tube.

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LEVEL 1 - 151 OF 225 PATENTS

4,363,769

<=2> GET 1st DRAWING SHEET OF 8

Dec. 14, 1982

Method for manufacturing thin and flexible ribbon wafer of semiconductor material and ribbon wafer

INVENTOR: Tsuya, Noboru, 1-38, Kashiwagi 2-Chome, Sendai City, Japan  
Arai, Kenichi, Sendai, Japan

... [\*18] extending parallel to a moving direction of the ejected melt so that at least two jet flows of some or different semiconductor material are simultaneously ejected through the holes so as to form a thin ribbon wafer or multi-layer type.

[\*19] 19. A method as defined in claim 1, wherein the raw semiconductor material is mixed with a substance selected from the group consisting of Ge, Si, Se, Te, PbS, InSb, ZnTe, PbSe, ...

PAGE 168

LEVEL 1 - 152 OF 225 PATENTS

4,362,597

<=2> GET 1st DRAWING SHEET OF 1

Dec. 7, 1982

Method of fabricating high-conductivity  
silicide-on-polysilicon structures for MOS devices

INVENTOR: Fraser, David B., Berkeley Heights, New Jersey  
Kinsbron, Eliezer, Highland Park, New Jersey  
Vratny, Frederick, Berkeley Heights, New Jersey

... [\*1] containing layer on top of said pattern and on said selected regions, the metallic constituent in said layer being selected from the group consisting of titanium, tantalum, molybdenum, tungsten, nickel and cobalt, which metal-containing layer is of the type that, upon sintering, will form a silicide,

lifting off said pattern thereby leaving on said device only the metal-containing layer deposited on said selected regions,

sintering said remaining metal- ...

... [\*4] top of said masking pattern and on said selected surface regions, the metallic constituent in said layer being selected from the group consisting of titanium, tantalum, molybdenum, tungsten, nickel and cobalt, which metal-containing layer is of the type that, upon sintering, will form a silicide,

removing said masking pattern from said polysilicon layer thereby lifting off those portions of said metal-containing layer deposited on top of said masking pattern and ...

... [\*5] masking pattern and on said surface regions of said polysilicon layer, the metallic constituent in said layer being selected from the group consisting of titanium, tantalum, molybdenum, tungsten, nickel and cobalt, which metal-containing layer is of the type that, upon sintering, will form a silicide,

removing said masking pattern from said intermediate layer thereby lifting off those portions of said metal-containing layer deposited on top of said masking pattern and ...

PAGE 169

LEVEL 1 - 153 OF 225 PATENTS

4,362,158

<=2> GET 1st DRAWING SHEET OF 2

Dec. 7, 1982

Synthetic bag-type container for human blood and its fractions, perfusion solutions, dialysis solutions and alimentary and chemical liquids in general

INVENTOR: Lena, Paolo, Via Castello, 13, 26038 Torre de'Picenardi (Cremona), Italy

... [\*3] two parallel side edges of the container.

[\*4] 4. A container as claimed in claim 1, particularly for containing solutions and liquids in general, wherein said initial film sheet is of the single-layer type, and is constituted by polyethylene-butyl rubber copolymer, polyethylene or polypropylene.

[\*5] 5. A container as claimed in claim 1, wherein the initial film sheet has a thickness of 80-150 microns.

[\*6] 6. ...

PAGE 170

LEVEL 1 - 154 OF 225 PATENTS

4,360,519

<=2> GET 1st DRAWING SHEET OF 4

Nov. 23, 1982

Thermal recording apparatus

INVENTOR: Saito, Tamio, Oume, Japan  
Fukumoto, Yoshikatsu, Hamura, Japan  
Tagaya, Kiyomi, Oume, Japan

... [\*5] respective switching group and capable of limiting the switching operation of said respective switching group.

[\*6] 6. A thermal recording apparatus according to claim 1, wherein said capacitor is an electrolytic capacitor of an electric double layer type construction.

[\*7] 7. A thermal recording apparatus according to claim 1, wherein said detecting means comprises two serially connected resistors in parallel with said capacitor; and a comparator means, coupled to ...

... [\*11] signals stored in said memory when the detected terminal voltage is less than the predetermined voltage.

[\*12] 12. A thermal recording apparatus according to claim 10, wherein said capacitor is an electrolytic capacitor of electric double layer type construction.

PAGE 171

LEVEL 1 - 155 OF 225 PATENTS

4,352,116

<=2> GET 1st DRAWING SHEET OF 7

Sep. 28, 1982



Solid state electro-optical devices on a semi-insulating substrate

INVENTOR: Yaviv, Amnon, San Marino, California  
Margalit, Shlomo, Pasadena, California  
Lee, Chien-Ping, Pasadena, California

... [\*15] matching parameters, with adjacent semi-conductor layers having different combinations of constituent elements and being of either of the N or P type, each of said layers including a region which is doped to a type opposite the layer's type whereby a PN junction is formed in the second layer; and

a first and second contacts on the top surface of the top third layer, said first contact being on the surface which is not doped and the second contact on the ...

PAGE 172

LEVEL 1 - 156 OF 225 PATENTS

4,341,686

Jul. 27, 1982

Adhesive products and a process for their use in polyurethanes

INVENTOR: Chakrabarti, Sarbananda, Ludwigshafen, Federal Republic of Germany  
Hutchison, John, Wachenheim, Federal Republic of Germany  
Volkert, Otto, Weisenheim, Federal Republic of Germany

... [\*6] by weight of a solvent mixture of cyclohexanone/methylene chloride in a weight ratio of approximately 50:50.

[\*7] 7. A process for improving the adhesiveness of cellular or noncellular polyurethanes to solid cover layers of all types wherein the improvement comprises treating the cover layers with an adhesive product comprising, based on the total weight,

(a) 1 to 10 percent by weight of an aminoalkyltrialkoxysilane,

(b) 1 to 20 percent by weight of a ...

PAGE 173

LEVEL 1 - 157 OF 225 PATENTS

4,337,216

<=2> GET 1st DRAWING SHEET OF 6

Jun. 29, 1982

Device in an evaporative cooler

INVENTOR: Korsell, Lars E. R., Stockholm, Sweden

... [\*1] socket being telescopically inserted only into another single corresponding opening in an adjacent contact body.

[\*2] 2. In an evaporative cooler including, a casing, at least one contact body of the multi-layer type located in said casing and formed with channels existing between the layers and which all are passed by air, and means for supplying water to selected channels in said body from above the body, the improvement comprising ...

PAGE 174

LEVEL 1 - 158 OF 225 PATENTS

4,305,670

Dec. 15, 1981

Liquid mixing device

INVENTOR: Moskowitz, Paul M., Brooklyn, New York  
Rushansky, Yuliy, Bronx, New York

... [\*1] surfaces of said disk extending in a plane perpendicular to the axis of rotation of said other shaft and being located symmetrically around said shaft,

said disk serving as a boundary layer type rotor in which boundary layer effects will occur along the surfaces of said disk during rotation of s disk, said boundary layer effect causing liquid to move in a downward, ...

PAGE 175

LEVEL 1 - 159 OF 225 PATENTS

4,288,992

<=2> GET 1st DRAWING SHEET OF 4

Sep. 15, 1981

Curtain for open front freezer or refrigerator

INVENTOR: Eliason, Carlyle R., 905 W. Inkster, Kalamazoo, Michigan 49008

... [\*16] flexible sheet curtain being extendible across said access opening near at least one of said strip curtain and said air curtain means to the opposite wall of said cabinet to form an air layer-type thermal barrier between said flexible sheet and strips when access to said access opening is not required.

[\*17] 17. The apparatus of claim 15, in which said upper front wall portion of said cabinet is ...

PAGE 176

LEVEL 1 - 160 OF 225 PATENTS

4,287,249

Sep. 1, 1981

Textured surface polypropylene film

INVENTOR: Eustance, John W., So. Glens Falls, New York  
Hobbs, Stanley Y., Scotia, New York  
Carley, Emilie L., Hartford, New York

... [\*1] properties for dielectric fluids which comprises a thin polypropylene film having one predetermined textured surface which is coextensively and uniformly covered by an overlapping pattern of fibroid irregularities comprising predominantly a stretched layer of Type I and Type II polypropylene crystal structure, and said film being characterized by a space factor of greater than about 5% and a haze measurement of greater than about 20%.

[\*2] 2. The film of ...  
LEVEL 1 - 161 OF 225 PATENTS

4,265,386

May 5, 1981

Torsional fluid damper system

INVENTOR: Levy, Avner, Irvine, California  
Karsh, Irving, Costa Mesa, California

... [\*12] a loop having a bight portion extending in contact with said circumferential wall of said container.

[\*13] 13. In a torsional fluid damper of the inertial mass and viscous fluid friction boundary layer type having a frequency response in the kHz region, the improvement comprising in combination:

means for containing an inertial mass and viscous fluid friction boundary layer comprising a rotatable container having an internal ...

LEVEL 1 - 162 OF 225 PATENTS

4,252,417

Feb. 24, 1981

Liquid crystal display

INVENTOR: Scheffer, Terry J., Forch, Switzerland  
Zeller, Hans R., Birr, Switzerland

What is claimed as new and desired to be secured by Letters Patent of the United States is:

[\*1] 1. A liquid crystal display comprising:

two parallel plates having inside surfaces on which are formed layer-type electrodes and between which is disposed a liquid crystal mixture to form a liquid crystal cell, said plates having outside surfaces on which no polarizers are disposed;

said liquid crystal mixture comprising primarily ...  
LEVEL 1 - 163 OF 225 PATENTS

4,243,708

<=2> GET 1st DRAWING SHEET OF 4

Jan. 6, 1981

Metallized textured surface polypropylene film

INVENTOR: Eustance, John W., South Glens Falls, New York  
Hobbs, Stanley Y., Scotia, New York  
Carley, Emilie L., Hartford, New York

... [\*1] properties for dielectric fluids which comprises a thin polypropylene film having one predetermined textured surface which is coextensively and uniformly covered by an overlapping pattern of fibroid irregularities comprising predominantly a stretched layer of Type I and Type II crystal structure, said film being characterized by a space factor of greater than about 5% and a haze measurement of greater than about 20%, and said film having an electrically ...

LEVEL 1 - 164 OF 225 PATENTS

4,231,754

Nov. 4, 1980

Chemiluminescent analytical device

INVENTOR: Vogelhut, Paul O., Mishawaka, Indiana

... [\*4] a photoresponsive layer in contact with at least one surface of said second layer which is in contact with the first layer.

[\*5] 5. The test device of claim 4 wherein the photoresponsive layer is a photoresponsive imaging layer of the type which is permanently transformed by exposure to a light response in proportion to the amount of light emitted.

[\*6] 6. A method for determination of a constituent in a sample which comprises contacting the sample with the....

LEVEL 1 - 165 OF 225 PATENTS

PAGE 181

4,229,095

<=2> GET 1st DRAWING SHEET OF 3

Oct. 21, 1980

Electro-optical color imaging apparatus

INVENTOR: Mir, Jose M., Webster, New York

... [\*5] produced so that the pixels of each successive strip are concurrently subjected to light of said different colors, sequentially and according to an image to be produced.

[\*6] 6. Electro-optical color imaging apparatus for use with an imaging layer of the type which can record different light colors, said apparatus comprising:

(a) means for disposing such an imaging layer in an imaging station of said apparatus;

(b) a plurality of discrete electro-optical ...  
LEVEL 1 - 166 OF 225 PATENTS

4,228,581

<=2> GET 1st DRAWING SHEET OF 1

Oct. 21, 1980

Method for producing semiconductor bodies having a defined edge profile which has been obtained by etching and is covered with a glass

INVENTOR: Chadda, Madan M., Nurnberg-Gaulnhofen, Federal Republic of Germany  
Maier, Reinhold, Nuremberg, Federal Republic of Germany

... [\*1] for producing semiconductor bodies having a glass-covered defined edge profile, said semiconductor bodies being obtained by etching from a large-area semiconductor basic wafer having a sequence of layer-type zones of different conductivity type with at least one pn-junction and a surface oxide layer thereon, the steps comprising

applying a etch-resistant protective coating onto said surface oxide layer,  
cutting ...

LEVEL 1 - 167 OF 225 PATENTS

PAGE 183

PAGE 182

4,223,234

<=2> GET 1st DRAWING SHEET OF 3

Sep. 16, 1980

Reduction of sparkle noise and mottling in CCD imagers

INVENTOR: Levine, Peter A., Trenton, New Jersey

... [\*4] B register responsive to applied multiple phase voltages for the storage in and transfer of charge along the channels of said B register;

said electrodes of said A and B registers being of the single layer type and comprising semiconductor material of one conductivity type and being separated from one another by "gaps" formed of semiconductor material of opposite conductivity type; and

a control electrode insulated from the electrodes of the A register and ...  
PAGE 184

LEVEL 1 - 168 OF 225 PATENTS

4,206,372

<=2> GET 1st DRAWING SHEET OF 2

Jun. 3, 1980

Reduction of sparkle noise in CCD imagers

INVENTOR: Levine, Peter A., Trenton, New Jersey

... [\*1] direction over the channels of said B register responsive to applied multiple phase voltages for the storage in and transfer of charge along the channels of said B register, said electrodes being of the single layer type and comprising semiconductor material of one conductivity type and being separated from one another by semiconductor material of opposite conductivity type;

a CCD C register including a semiconductor formed with a ...  
185

LEVEL 1 - 169 OF 225 PATENTS

4,160,684

<=2> GET 1st DRAWING SHEET OF 3

Jul. 10, 1979

Method of manufacturing a coalescing demister

PAGE

INVENTOR: Berger, Jr., L. Joseph, Birmingham, Michigan  
Guequierre, Denis D., Birmingham, Michigan

... [\*4] said cloth into place, thereby forming an anti-migration filter layer.

[\*5] 5. The method described in claim 4, and including the step of placing a screen type retainer inside said anti-migration layer of the type adapted to assert pressure on said anti-migration and said drain layers and keep them in intimate contact with one another and with said inner retainer.

[\*6] 6. The method described in claim 5, and including the ...

... [\*8] said cloth into place thereby forming an anti-migration filter layer.

[\*9] 9. The method described in claim 8, and including the step of placing a screen-type retainer inside said anti-migration layer of the type adapted to assert pressure on said anti-migration and said drain layers and keep them in intimate contact with one another and with said inner coalescer retainer.

[\*10] 10. The method described in claim 9, and ...  
LEVEL 1 - 170 OF 225 PATENTS

PAGE 186

4,150,186

<=2> GET 1st DRAWING SHEET OF 2

Apr. 17, 1979

Composite board structure and a method of and an apparatus  
for producing the board structure

INVENTOR: Kazama, Norio, Yokohama, Japan

... [\*7] copolymers, and ethylene-vinyl acetate copolymers.

[\*8] 8. A composite board structure as set forth in claim 1, in which the respective thermoplastic adhesive materials forming said first and second layers are of the types which are homogeneous to each other.

[\*9] 9. A composite board structure as set forth in claim 1, having a three-dimensionally curved portion.

LEVEL 1 - 171 OF 225 PATENTS

PAGE 187

4,137,077

<=2> GET 1st DRAWING SHEET OF 1

Jan. 30, 1979

Broadening the spatial frequency pass band of a thermoplastic layer

INVENTOR: Credelle, Thomas L., East Windsor, New Jersey  
Hannan, William J., Palm Beach Gardens, Florida  
Spong, Fred W., Lawrenceville, New Jersey

... [\*1] first and second surfaces respectively connected to a surface of a substrate and to one surface of a photoconductor layer that is adapted to receive an interference pattern of light representative of an image, the improvement comprising a thermoplastic layer of the type that has a frost frequency inversely related to thickness, said thermoplastic layer having a surface with undulations that cause said thermoplastic layer to have a multiplicity of frost frequencies, said undulations having a spatial frequency ...

... [\*4] less than 100 cycles per millimeter.

[\*5] 5. In a holographic recording medium wherein one surface of an electrically conductive layer is connected to a surface of a substrate, the improvement comprising a photoplastic layer of the type that has a frost frequency inversely related to thickness, said photoplastic layer having a surface with undulations that cause said photoplastic layer to have a multiplicity of frost frequencies, said undulations having a spatial frequency ...

PAGE 188

LEVEL 1 - 172 OF 225 PATENTS

4,135,291

<=2> GET 1st DRAWING SHEET OF 2

Jan. 23, 1979

Method for producing semiconductor devices with high reverse blocking capability

INVENTOR: Tursky, Werner, Schwabach, Eichvasen, Federal Republic of Germany  
Chadda, Madan, Nuremberg-Gaulnhofen, Federal Republic of Germany  
Schafer, Horst, Zirndorf, Federal Republic of Germany

... [\*1] method for producing a plurality of semiconductor devices out of a semiconductor disc of a first conductivity type with the devices having a high reverse blocking capability and having a sequence of at least three layer-type zones of different conductivity types, of which at least one is highly resistive, and at least one pn-junction, comprising the steps of:

forming grooves of a depth at least equal to the desired thickness of the highly resistive zone ...

... [\*1] said disc into sections of smaller areal expanse capable of being separated into individual semiconductor device containing wafers;



thereafter subjecting the disc to a diffusion process to produce a sequence of at least three layer-type zones of different conductivity which form at least one pn-junction in each said section, and a zone of a single conductivity type which passes through the entire disc in the profile region of ...

... [\*2] a diffusion process includes diffusing an impurity which forms a zone of the opposite conductivity type into both major surfaces of said disc to provide, in each said section, a sequence of three layer-type zones of alternating conductivity types with the zones adjacent both major surfaces being of said opposite conductivity type and an inner zone of said first conductivity type, and to provide a zone of said opposite ...

LEVEL 1 - 173 OF 225 PATENTS

4,120,700

<=2> GET 1st DRAWING SHEET OF 2

Oct. 17, 1978

Method of producing p-n junction type elements by ionized  
cluster beam deposition and ion-implantation

INVENTOR: Morimoto, Kiyoshi, Mobara, Japan

... [\*1] substrate electrode being formed of a metal film such as can produce an ohmic contact with the semiconductor layer of the one impurity type;

ionizing impurity atoms such as can form a semiconductor layer having the type of conductivity opposite to that of the semiconductor layer of the one impurity type;

accelerating the impurity ions by giving them kinetic energies;

implanting the impurity ions in the semiconductor layer of the one impurity type to form an ion- ...

... [\*2] substrate electrode being formed of a metal film such as can produce an ohmic contact with the semiconductor layer of the one impurity type;

ionizing impurity atoms such as can form a semiconductor layer having the type of conductivity opposite to that of the semiconductor layer of the one impurity type;

accelerating the impurity ions by giving them kinetic energies;

implanting the impurity ions in the semiconductor layer of the one impurity type to form an ion- ...

... [\*3] substrate electrode being formed of a metal film such as can produce an ohmic contact with the semiconductor layer of the one impurity type;

ionizing impurity atoms such as can form a semiconductor layer having the type of conductivity opposite to that of the semiconductor layer of the one impurity type;

accelerating the impurity ions by giving them kinetic energies;

implanting the impurity ions in the semiconductor layer of the one impurity type to form an ion- ...

... [\*4] substrate electrode being formed of a metal film such as can produce an ohmic contact with the semiconductor layer of the one impurity type;

ionizing impurity atoms such as can form a semiconductor layer having the type of conductivity opposite to that of the semiconductor layer of the one impurity type;

Pat. No. 4120700, \*4

accelerating the impurity ions by giving them kinetic energies;

implanting the impurity ions in the semiconductor layer of the one impurity type to form an ion- ...

LEVEL 1 - 174 OF 225 PATENTS

4,119,142

<=2> GET 1st DRAWING SHEET OF 2

Oct. 10, 1978

Arrangement for transferring heat from the exhaust air  
leaving an enclosed volume to the input air supplied to said  
volume

INVENTOR: Margen, Peter Heinrich Erwin, Nykoping, Sweden

... [\*1] circuit, arranged in said supply conduit, a second heat exchanger in said circuit, arranged in said exhaust conduit, the improvement comprising a heat store of the stratified liquid-layer type, the hot side of which is coupled to the hot side of the circuit and the cold side of which is coupled to the cold side of said circuit, valve means for deflecting part of the hot circuit liquid into said store during normal ...

... [\*2] least one by-pass line arranged in said circuit in parallel with said second heat exchanger;

means for controlling the liquid flow through said second heat exchanger; and,

layer type heat store means for supplying heat to said first heat exchanger in the form of heat extracted from said exhaust air, while said second heat exchanger is disconnected for defrosting, having the ...

LEVEL 1 - 175 OF 225 PATENTS

4,096,389

<=2> GET 1st DRAWING SHEET OF 5

Jun. 20, 1978

Apparatus for minimizing radiation exposure and improving resolution in radiation imaging devices

INVENTOR: Ashe, John B., Palatine, Illinois  
Williams, Gwilym H., Palatine, Illinois  
Sypal, Kenneth L., Glen Ellyn, Illinois

... [\*6] improvement as defined in claim 1, wherein said sandwich assembly comprises a plurality of substantially equally spaced concentric cylindrical layers of alternating attenuation and spacing material, each said respective layer type being substantially uniform in length and in thickness, whereby a circular beam pattern is produced.

[\*7] 7. The improvement as defined in claim 1, wherein said sandwich assembly comprises a layer of ...

LEVEL 1 - 176 OF 225 PATENTS

4,092,663

<=2> GET 1st DRAWING SHEET OF 2

May 30, 1978

Semiconductor device

INVENTOR: Schafer, Horst, Zirndorf-Nuremberg, Germany, Federal Republic of

I claim:

[\*1] 1. In a semiconductor device with a high blocking capability comprising a semiconductor wafer having at least two layer type zones of alternatingly opposite conductivity type and different doping concentrations and forming a pn junction therebetween which intersects the edge surface of the semiconductor wafer, the higher doped of said at least two zones forming ...

PAGE 194

LEVEL 1 - 177 OF 225 PATENTS

4,087,159

<=2> GET 1st DRAWING SHEET OF 15

May 2, 1978

Self imaging system using a waveguide

INVENTOR: Ulrich, Reinhard, Leonberg-Silberberg, Germany, Federal Republic of

... [\*24] provided at an input window (E1) in FIG. 31) taking up the one half of the input surface of the waveguide.

[\*25] 25. An imaging system according to claim 24, characterized by the feature that the waveguide is a layer type waveguide, which has a different thickness in the region (PS) of the input window (E1) than in the other regions.

[\*26] 26. An imaging system according to claim 24, characterized by the feature that the phase shift device ( ...

LEVEL 1 - 178 OF 225 PATENTS

4,084,863

<=2> GET 1st DRAWING SHEET OF 1

Apr. 18, 1978

Bearing and bearing liner having a compliant layer

INVENTOR: Capelli, Alfred J., Palos Verdes Peninsula, California

... [\*1] height of the projection on the substrate.

[\*2] 2. In a bearing including a substrate having an irregular surface and further including a thin and deformable wear resistant layer having a wear surface wherein the wear resistant layer is of the type which would be deformed by the irregular surface of the substrate upon loading of the wear resistant layer against the irregular surface, the wear resistant layer including a porous backing member and particles of a lubricant ...

LEVEL 1 - 179 OF 225 PATENTS

4,037,244

<=2> GET 1st DRAWING SHEET OF 2

Jul. 19, 1977

Avalanche photodiode

INVENTOR: de Cremoux, Baudouin, Paris, France

... [\*4] 3, wherein the thickness of the third layer is sufficiently thin to be transparent to the radiation, the radiation being absorbed in the first layer.

[\*5] 5. A diode as claimed in claim 4, wherein said first layer has type n-conductivity, said second and third layers having type p-conductivity, the first layer having a doping concentration of the order of  $10^{16} > \text{at/cm}^3$ ,

said second and said third layers having doping concentrations of the order of  $10^{19} > \text{at/cm}^3$ , the thickness of the ...

... [\*6] 3, wherein said third layer is sufficiently thick to absorb the radiation to be detected.

[\*7] 7. A diode as claimed in claim 6, wherein the first layer has p-type conductivity, the second and third layers have type n-conductivity, the doping concentrations being of the order of  $10^{18} > \text{at/cm}^3$  and  $10^{16} > \text{at/cm}^3$ , respectively.

[\*8] 8. A diode as claimed in claim 1, wherein the layers are made of ...  
PAGE 197

LEVEL 1 - 180 OF 225 PATENTS

4,019,843

<=2> GET 1st DRAWING SHEET OF 4

Apr. 26, 1977

Film blowhead for producing tubular film

INVENTOR: Zimmermann, Werner Josef, Lengerich of Westphalia, Germany

... [\*3] in each of said pairs disposed in a common radial plane and with the radial planes in parallel relationship.

[\*4] 4. A film blowhead according to claim 1 wherein the film blowhead is of multi-layer type and wherein said air inlet and outlet tubes are disposed between said axial passage portions of said distributing passages in at least one radial plane.

LEVEL 1 - 181 OF 225 PATENTS

4,015,034

<=2> GET 1st DRAWING SHEET OF 2

Mar. 29, 1977

Register for index marking article

INVENTOR: Smolen, Benjamin Edward, 1501 Broadway, New York, New York 10036

... [\*2] said carrier includes an adhesive surface on the face opposite said release surface for securing said carrier to a said sheet.

[\*3] 3. Article in accordance with claim 1 wherein said adhesive layer is of the type having an initial low tack which is rendered highly adherent responsive to localized high pressure such as exerted by a stylus scanned in registry therewith.

4. Article in accordance with claim 3 wherein said ...

LEVEL 1 - 182 OF 225 PATENTS

4,012,817

<=2> GET 1st DRAWING SHEET OF 1

Mar. 22, 1977

Method of making a capacitor

INVENTOR: Preissinger, Karl-Heinz, Taufkirchen, Germany, Federal Republic of  
Wehnelt, Ulrich, Starnberg, Germany, Federal Republic of

We claim as our invention:

[\*1] 1. A method for producing a layer type capacitor comprising the steps  
of

coating an adhesion-imparting layer in a dissolved state onto a first  
covering foil,

applying a first conductive layer with pores therein into the exposed surface  
of said adhesion- ...

... [\*1] sides by pressing heated leads at least at one point through said

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To: dmorris@watson.ibm.com  
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covering foil and the respective of said layers into said first covering foil.

[\*2] 2. A method for producing a layer type capacitor in accordance with claim 1 wherein the hardening glue is added to the adhesion-imparting layer in a concentration which does not prevent activation of said adhesion-imparting layer by penetration of the dielectric solvent ...

PAGE 200

LEVEL 1 - 183 OF 225 PATENTS

3,969,232

<=2> GET 1st DRAWING SHEET OF 1

Jul. 13, 1976

Bearing and bearing liner wear resistant compliant layer

INVENTOR: Turner, Peter H., Burbank, California

... [\*2] mixture including the adhesive.

[\*3] 3. In a bearing including a substrate having an irregular surface,

a first thin wear resistant layer having a first wear surface wherein the first wear resistant layer is of the type which would be deformed by the irregular surface of the substrate upon loading of the first wear resistant layer against the irregular surface, the first wear resistant layer including a first porous backing member and ...

LEVEL 1 - 184 OF 225 PATENTS

3,958,484

<=2> GET 1st DRAWING SHEET OF 1

PAGE 201

May 25, 1976

Sealing means for wind instruments

INVENTOR: Nelson, Robert E., Los Angeles, California  
Gilbert, Robert D., Los Angeles, California

... [\*4] layer.

[\*5] 5. In the sealing means of claim 4 wherein said first layer is Volara material and said second layer is Volite material.

[\*6] 6. In the sealing means of claim 5 wherein said first layer is Type A Volara material.

[\*7] 7. In the sealing means of claim 6 wherein a third layer of material having indicia thereon is adhered to said second layer, said third layer being fixedly secured to said ...

... [\*12] first layer is laminated to said second layer.

[\*13] 13. The pad of claim 12 wherein said first layer is Volara material and the second layer is Volite material.

[\*14] 14. The pad of claim 13 wherein said first layer is Type A Volara material.

[\*15] 15. The pad of claim 14 wherein a third layer of material having indicia thereon is adhered to said second layer.

LEVEL 1 - 185 OF 225 PATENTS

3,956,624

<=2> GET 1st DRAWING SHEET OF 2

May 11, 1976

Method and device for the storage and multiplication of  
analog signals

INVENTOR: Audaire, Luc, St-Nizier-du-Moucherotte, France  
Borel, Joseph, Echirolles, France  
LE Goascoz, Vincent, Claix, France  
Poujois, Robert, Grenoble, France

... [\*1] ordered series is derived from the sampling of a function, wherein a multiplication of two corresponding terms is performed by recording the signal which is proportional to one sample of said function in a memory of the multiple dielectric layer type and by applying a given voltage to the gate of said transistor so as to generate a signal which is a linear function of the threshold voltage which is in turn a linear function of the writing signal at



the input of ...

PAGE 203

LEVEL 1 - 186 OF 225 PATENTS

3,949,463

<=2> GET 1st DRAWING SHEET OF 2

Apr. 13, 1976

Method of applying an anti-reflective coating to a solar  
cell

INVENTOR: Lindmayer, Joseph, Bethesda, Maryland  
Allison, James F., Silver Springs, Maryland

... [\*1] as a solar cell, an anti-reflective coating and a desired pattern  
of a metal electrode for current collection, comprising the steps of:

a. coating said surface with a first metal layer of the type which can be  
oxidized to form said anti-reflective coating,

b. forming on top of said coating a metal electrode having said desired  
pattern, said first metal layer having parts thereof exposed which are ...

PAGE 204

LEVEL 1 - 187 OF 225 PATENTS

3,939,642

<=2> GET 1st DRAWING SHEET OF 4

Feb. 24, 1976

Electronic timepiece semiconductor intergrated circuit

INVENTOR: Morozumi, Shinji, Nagano, Japan

... [\*4] substrate is formed of a material selected from the group  
consisting of sapphire, spinel, silicon oxide or titanium oxide.

[\*5] 5. An electronic timepiece as claimed in claim 3 wherein the P-channel  
transistors are depletion-layer type transistors and the N-channel transistors  
are reverse-layer type transistors.

[\*6] 6. An electronic timepiece as claimed in claim 3, wherein said  
P-channel and N-channel transistors are reverse-layer channel transistors.

[\*7] 7. An electronic timepiece, as claimed in ...  
LEVEL 1 - 188 OF 225 PATENTS

3,936,730

<=2> GET 1st DRAWING SHEET OF 1

PAGE 205

Feb. 3, 1976

Insulation test apparatus including improved means for simultaneous display

INVENTOR: Pittman, Paul F., Pittsburgh, Pennsylvania

... [\*3] branches is a current transformer and said means for displaying signals is an oscilloscope.

[\*4] 4. The subject matter of claim 2 wherein:

said switching means comprises a plurality of semiconductor switching devices of the four layer type connected in a series string and provided with means to trigger said series string to conduction to effect discharge of said capacitor.

[\*5] 5. The subject matter of claim 1 wherein:

said means for displaying ...  
LEVEL 1 - 189 OF 225 PATENTS

3,930,903

<=2> GET 1st DRAWING SHEET OF 1

Jan. 6, 1976

Stabilized superconductive wires

INVENTOR: Randall, Robert N., Wayland, Massachusetts  
Wong, James, Wayland, Massachusetts

What is claimed is:

[\*1] 1. Superconductive multi-filament wire product comprising,  
means defining a copper matrix with a plurality of spaced filaments therein,

each of the filaments comprising a layer therein of type II superconducting intermetallic compound of Beta-Wolfram structure, being the diffusion reaction product of source filaments comprising a cross-section multilayer configuration of a refractory metal layer each containing ...

LEVEL 1 - 190 OF 225 PATENTS

3,929,849

<=2> GET 1st DRAWING SHEET OF 1

Dec. 30, 1975

Tetraalkyl phosphonium aluminosilicates

INVENTOR: Oswald, Alexis A., Mountainside, New Jersey

What is claimed is:

[\*1] 1. Tetra-alkyl phosphonium clays of layer and chain type structure.

[\*2] 2. Tetra-alkyl phosphonium clays of layer type structure.

[\*3] 3. The compositions of claim 2 wherein said layer type clay is a montmorillonite.

[\*4] 4. Tetra-alkyl phosphonium clays of the formula  $[R_4P + ]$  Clay -

wherein R is a C1 to C100 aliphatic hydrocarbyl group, and the clay is a negatively charged aluminosilicate of layer and chain ...

... [\*8] C1 to C7 low aliphatic groups and C8 to C100 high aliphatic groups in such a manner that if R' is low, R'' should be high and the reverse; Clay - is a negatively charged layered aluminosilicate of layer type structure.

[\*9] 9. The composition of claim 8 wherein the high aliphatic groups equal C8 to C40 alkyl and the low C1 to C7 aliphatic groups are selected from the group consisting of alkyl, alkenyl and alkynyl.

[\*10] 10. The composition of ...  
LEVEL 1 - 191 OF 225 PATENTS

3,922,777

<=2> GET 1st DRAWING SHEET OF 1

Dec. 2, 1975

Process for the production of layer circuits with conductive layers on both sides of a ceramic substrate

INVENTOR: Weitze, Artur, Pullach, Germany, Federal Republic of  
Leskovar, Peter, Munich, Germany, Federal Republic of

We claim as our invention:

[\*1] 1. A process for the production of layer-type printed circuits having conductive layers on both sides of a ceramic substrate which comprises providing an aperture in a green ceramic substrate, inserting into said aperture, a high melting metal pin having ...

LEVEL 1 - 192 OF 225 PATENTS

3,922,567

<=2> GET 1st DRAWING SHEET OF 5

Nov. 25, 1975

Integrated IGFET bucket-brigade circuit

INVENTOR: Adam, Fritz G., Freiburg, Germany, Federal Republic of  
Obermeier, Cornelius, Freiburg, Germany, Federal Republic of  
Scheffer, Gerhard, Denzlingen, Germany, Federal Republic of  
Wilmsmeyer, Klaus, Denzlingen, Germany, Federal Republic of

... [\*1] sources of clock pulses, said first source coupled to said even-numbered transistors and said second source coupled to said odd-numbered transistors; and

a row of field-effect transistors of the depletion-layer type having source and drain regions, said field-effect transistors employing gate electrodes on an insulated-gate layer, wherein the last transistor in said row is provided with an electrical terminal to which said source of operating voltage is ...

PAGE 210

LEVEL 1 - 193 OF 225 PATENTS

3,910,802

<=2> GET 1st DRAWING SHEET OF 1

Oct. 7, 1975

Stabilized superconductors

INVENTOR: Wong, James, Wayland, Massachusetts

What is claimed is:

[\*1] 1. Superconductive multi-filament wire product comprising, means defining a bronze matrix with a plurality of spaced filaments therein,

each of the filaments comprising a layer of type II superconducting intermetallic compound of Beta-Wolfram structure being the diffusion reaction product of a first elemental component derived from said bronze matrix and of a second elemental component derived from source ...

LEVEL 1 - 194 OF 225 PATENTS

3,895,336

<=2> GET 1st DRAWING SHEET OF 1

Jul. 15, 1975

Transformer core with composite offset V-miter and step joint

INVENTOR: Pitman, Frank A., Rome, Georgia

I claim:

[\*1] 1. In a transformer core of the stacked flat-layer type having a plurality of flat, laminated, layered members of equal width, each of said members including;

two generally rectangular shaped, parallel, spaced-apart, outside leg members beveled at each end;

...

LEVEL 1 - 195 OF 225 PATENTS

3,895,335

<=2> GET 1st DRAWING SHEET OF 1

Jul. 15, 1975

Series/parallel connected single phase power transformer

INVENTOR: Manimalethu, Abraham I., Peru, Massachusetts

... [\*2] consists of two high voltage windings and two low voltage windings.

[\*3] 3. A single phase electrical power transformer as defined in claim 2 wherein said high voltage windings are of the layer type, the low voltage windings between high voltage windings is of the helical type and the remaining low voltage winding is of the layer type.

[\*4] 4. A single phase electrical power transformer as defined in claim 2 wherein said high voltage windings are of the layer type, the low voltage windings between high voltage windings is of the helical type and the remaining low voltage winding is of the disc type.

[\*5] 5. A single phase electrical power transformer as defined in claim 2 wherein said high voltage windings are of the disc type, the low voltage winding between high voltage windings of the helical type and the remaining low voltage winding is of the layer type.

[\*6] 6. A single phase electrical power transformer as defined in claim 2 wherein said high voltage windings are of the disc type, the low voltage winding between the high voltage windings is of the ...

LEVEL 1 - 196 OF 225 PATENTS

3,892,655

Jul. 1, 1975

Layered clay minerals, catalysts, and processes for using

INVENTOR: Hickson, Donald A., Richmond, California

What is claimed is:

[\*1] 1. A hydroconversion process comprising contacting a hydrocarbon feedstock at conventional hydroconversion conditions with a catalyst comprising: (1) a layer-type trioctahedral, clay-like mineral, and (2) at least one hydrogenation component, said mineral having prior to dehydrating and calcining of said catalyst, the empirical formula:  
MgO : SSiO2 : aAl2O3: bAB : xH2O

wherein the layer-lattice ...

... [\*9] claim 1 wherein said hydrogenation component comprises platinum.

[\*10] 10. A catalytic conversion process comprising contacting a hydrocarbon feedstock at conventional catalytic conversion conditions with a catalyst comprising a layer-type trioctahedral, clay-like mineral, said mineral having prior to dehydrating and calcining of said catalyst the empirical formula:

MgO : SSiO2 : aAl2O3 : bAB : xH2O

wherein the layer-lattice structure is composed of said silica, said ...

PAGE 214

LEVEL 1 - 197 OF 225 PATENTS

3,888,678

Jun. 10, 1975

Method for adjusting triboelectric charging characteristics  
of materials

INVENTOR: Bailey, Jr., William J., Rochester, New York  
Houle, James F., Rochester, New York  
Van Norman, Gilden R., Rochester, New York

... [\*50] agent has the following empirical structure:

[\*51] 51. The film base element of claim 50 further including Saponin.

[\*52] 52. A film base element suitable for the reception of at least one radiation sensitive layer and of the type subject to triboelectric charging upon impact and dissociation with another usually dissimilar material said element having a surface thereof modified against generation of triboelectrical charges sufficient in electrical potential to cause static ...  
LEVEL 1 - 198 OF 225 PATENTS

3,887,454

<=2> GET 1st DRAWING SHEET OF 1

Jun. 3, 1975

Layered clay minerals and processes for using

INVENTOR: Hickson, Donald A., Richmond, California

What is claimed is:

[\*1] 1. A hydroconversion process comprising contacting a hydrocarbon feedstock at conventional hydroconversion conditions with a catalyst comprising (1) a layer-type dioctahedral, clay-like mineral, and (2) at least one hydrogenation component, said mineral having prior to dehydrating and calcining of said catalyst, the empirical formula:  
MgO : sSiO<sub>2</sub> : aAl<sub>2</sub>O<sub>3</sub> : bAB : xH<sub>2</sub>O

wherein the layer-lattice ...

... [\*9] claim 1 wherein said hydrogenation component comprises platinum.

[\*10] 10. A catalytic conversion process comprising contacting a hydrocarbon feedstock at conventional catalytic conversion conditions with a catalyst comprising a layer-type dioctahedral, clay-like mineral, said mineral having prior to dehydrating and calcining of said catalyst the empirical formula:

MgO : sSiO<sub>2</sub> : aAl<sub>2</sub>O<sub>3</sub> : bAB : xH<sub>2</sub>O

wherein the layer-lattice structure is composed of said silica, said ...

PAGE 216

LEVEL 1 - 199 OF 225 PATENTS

3,884,539

<=2> GET 1st DRAWING SHEET OF 1

May 20, 1975

Method of making a multialkali electron emissive layer

INVENTOR: Sommer, Alfred Hermann, Princeton, New Jersey

I claim:

[\*1] 1. A method of activating a multialkali electron-emissive cathode layer, of the type wherein a layer of antimony is exposed at elevated temperature, within an evacuated body, to vapors of a plurality of alkali metals including cesium, to form an electron-emissive compound, wherein the improvement comprises:

exposing the cathode layer to ....

LEVEL 1 - 200 OF 225 PATENTS

3,875,288

Apr. 1, 1975

Production of synthetic silicate minerals

INVENTOR: Hoffman, George W., Houston, Texas  
Blankenship, H. Michael, Houston, Texas  
Granquist, William T., Houston, Texas

Having described the invention, we claim:

[\*1] 1. The process of producing a 2:1 layer-type clay-like mineral product having the empirical formula:  
 $n\text{SiO}_2:\text{Al}_2\text{O}_3:\text{mAB}:\text{xH}_2\text{O}$

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 1.7 to 3.0,

m is from 0.2 to 0.6,

...

LEVEL 1 - 201 OF 225 PATENTS

3,864,931

PAGE 218

<=2> GET 1st DRAWING SHEET OF 1

Feb. 11, 1975

PROCESS AND APPARATUS FOR FOOD FREEZING

INVENTOR: Guttinger, Manfred, Leinfelden, Germany, Federal Republic of

... [\*11] second flow than for said first flow.

[\*12] 12. Process for freezing foodstuffs comprising the successive steps of:

placing foodstuffs in a substantially flat layer on a substantially horizontal support, which layer is of the type which would exert such a resistance against the through flow of a medium from above that it would be extremely difficult for the medium to flow through the layer and through the support which has a plurality of spaced openings extending therethrough,

...

LEVEL 1 - 202 OF 225 PATENTS

3,864,726

PAGE 219

<=2> GET 1st DRAWING SHEET OF 1



Feb. 4, 1975

CONTROLLABLE SEMICONDUCTOR RECTIFIER

INVENTOR: Semikron Gesellschaft fur Gleichrichterbau und Elektronik m.b.H.,  
Zirndorf, Germany, Federal Republic of

I claim:

[\*1] 1. In a controllable semiconductor rectifier device including: a monocrystalline semiconductor body having planar major outer surfaces and four layer-type zones of alternatingly opposite conductivity types with the one of the inner zones of said semiconductor body which serves as the base zone, and which is adjacent to the one of the outer zones of said semiconductor body which serves as the emitter ...

LEVEL 1 - 203 OF 225 PATENTS

3,858,236

<=2> GET 1st DRAWING SHEET OF 2

Dec. 31, 1974

FOUR LAYER CONTROLLABLE SEMICONDUCTOR RECTIFIER WITH  
IMPROVED FIRING PROPAGATION SPEED

INVENTOR: Schafer, Horst, Zirndorf, Germany, Federal Republic of  
Herbing, Lothar, Nurnberg, Germany, Federal Republic of

We claim:

[\*1] 1. In a controllable semiconductor rectifier device including: a monocrystalline semiconductor body having four layer-type zones of alternatingly opposite conductivity types and with the one of the inner zones of said semiconductor body which borders on the one of the outer zones of said semiconductor body which serves as the emitter zone of the device having a portion thereof which is to ...

LEVEL 1 - 204 OF 225 PATENTS

3,854,983

Dec. 17, 1974

FLAMEPROOF COVERING MATERIAL, SUCH AS TICKING

INVENTOR: Brodnyan, John G., Langhorne, Pennsylvania

I claim:

[\*1] 1. A cover fabric of composite-layer type comprising a light-weight woven or damask fabric, a soft, flexible layer adhered thereto formed of a

PAGE 220

PAGE 221

crushed foam of a polymeric material and a metal-containing coating of about 0.5  
to ...

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LEVEL 1 - 205 OF 225 PATENTS

3,849,217

<=2> GET 1st DRAWING SHEET OF 6

Nov. 19, 1974

METHOD OF MANUFACTURING HIGH FREQUENCY DIODE

INVENTOR: Kroger, Harry, Sudbury, Massachusetts  
Potter, Curtis N., Holliston, Massachusetts

We claim:

[\*1] 1. The method of making a high frequency diode device from a body of semiconductor material having type n + conductivity and having an epitaxial layer of type n conductivity, the method comprising:

forming a layer of type p conductivity material at a surface of said epitaxial layer,

forming a metal layer of chromium over said surface,

forming a metal layer of gold over said chromium layer,

...

... [\*4] contiguous metal ring layers by etching, and  
removing said mask.

[\*5] 5. The method of making a high frequency diode device from a body of semiconductor material having type n + conductivity and an epitaxial layer having type n conductivity, the method comprising:

forming a layer of type p conductivity material at a first free surface of said epitaxial layer,

forming a base layer of gold at a second free surface of said type n + semiconductor material,

forming ...

LEVEL 1 - 206 OF 225 PATENTS

3,844,979

Oct. 29, 1974

LAYERED CLAY MINERALS, CATALYSTS, AND PROCESSES FOR USING

PAGE 223

INVENTOR: Hickson, Donald A., Richmond, California

What is claimed is:

[\*1] 1. A layer-type, trioctahedral, clay-like mineral having the empirical formula

MgO : sSiO<sub>2</sub> : aAl<sub>2</sub>O<sub>3</sub> : bAB : xH<sub>2</sub>O

wherein the layer-lattice structure is composed of said silica, said alumina, said magnesia, said A and B, and wherein

s is from ...

... [\*5] hydrogen form, wherein  $s = 1.166 a = 0.08$ , and said mineral having after calcination a fluoride content of from 1 to 3 weight percent.

[\*6] 6. A catalytic cracking catalyst comprising dehydrated, calcined, layer-type, trioctahedral, clay-like mineral having prior to dehydration and calcining of said catalyst the empirical formula  
MgO : sSiO<sub>2</sub> : aAl<sub>2</sub>O<sub>3</sub> : bAB : xH<sub>2</sub>O

wherein the layer-lattice structure is composed of said silica, said alumina, said ...

... [\*7] dehydrated mineral is composited with an amorphous inorganic oxide.

[\*8] 8. The catalytic cracking catalyst of claim 6 wherein said dehydrated mineral is composited with a zeolite.

[\*9] 9. A catalyst composite comprising:

A. a layer-type, trioctahedral, clay-like mineral having prior to dehydration and calcining of said catalyst the empirical formula  
MgO : sSiO<sub>2</sub> : aAl<sub>2</sub>O<sub>3</sub> : bAB : xH<sub>2</sub>O

wherein the layer-lattice structure is composed of said silica, said alumina, said ...

LEVEL 1 - 207 OF 225 PATENTS

3,844,978

<=2> GET 1st DRAWING SHEET OF 1

Oct. 29, 1974

LAYERED CLAY MINERALS AND PROCESSES FOR USING

INVENTOR: Hickson, Donald A., Richmond, California

What is claimed is:

[\*1] 1. A layer-type, dioctahedral, clay-like mineral having the empirical formula  
MgO : SSiO2 : aAl2O3 : bAB : xH2O

wherein the layer-lattice structure is composed of said silica, said alumina, said magnesia, said A and said B, and wherein

...

... [\*5] hydrogen form, wherein  $s = 3.28$ ,  $a = 0.74$ , and said mineral having after calcination a fluoride content of from 1 to 3 weight percent.

[\*6] 6. A catalytic cracking catalyst comprising dehydrated, calcined, layer-type, dioctahedral, clay-like mineral having prior to dehydration and calcining of said catalyst the empirical formula  
MgO : SSiO2 : aAl2O3 : bAB : xH2O

wherein the layer-lattice structure is composed of said silica, said alumina, said ...

... [\*7] dehydrated mineral is composited with an amorphous inorganic oxide.

[\*8] 8. The catalytic cracking catalyst of claim 6 wherein said dehydrated mineral is composited with a zeolite.

[\*9] 9. A catalyst composite comprising:

A. a layer-type, dioctahedral, clay-like mineral having prior to dehydration and calcining of said catalyst the empirical formula  
MgO : SSiO2 : aAl2O3 : bAB : xH2O

wherein the layer-lattice structure is composed of said silica, said alumina, said ...  
PAGE 225

LEVEL 1 - 208 OF 225 PATENTS

3,818,248

<=2> GET 1st DRAWING SHEET OF 2

Jun. 18, 1974

SERIALLY CONNECTED SEMICONDUCTOR SWITCHING DEVICES  
SELECTIVELY CONNECTED FOR PREDETERMINED VOLTAGE BLOCKING AND  
RAPID SWITCHING

INVENTOR: Pittman, Paul F., Pittsburgh, Pennsylvania

... [\*1] minimizes the turn on time of said first number of devices.

[\*2] 2. The subject matter of claim 1 wherein: said voltage varies over a range of at least an order of magnitude; said switching devices are of the four layer type; said means for selectively connecting is such that said second number of said switching devices is in two groups of approximately equal size at the ends of the series connection.

[\*3] 3. The subject matter of claim 1 wherein: ...  
LEVEL 1 - 209 OF 225 PATENTS

3,816,343

Jun. 11, 1974

KAOLINITE COATED WITH SYNTHESIZED LAYER-TYPE SILICATE  
MINERALS

INVENTOR: Hoffman, George W., Houston, Texas  
Granquist, William T., Houston, Texas

Having described the invention, we claim:

[\*1] 1. The process of preparing a synthetic layer-type mineral-kaolinite complex which consists in commingling kaolinite with a reaction mixture consisting essentially of:

water;

a minor proportion of alumina;

silica in the molar ratio to said alumina of 2.7 to 3.3; and

...

... [\*1] alumina of 0.2 to 0.6;

thereafter autoclaving the mixture thus formed at a temperature within the range of 280° to 315°C. for a period of time sufficient for said reaction mixture to be converted to a layer-type clay-like mineral;

and cooling said mixture and recovering said complex therefrom.

[\*2] 2. The process in accordance with claim 1 wherein the weight ratio of solids in said reaction mixture to said kaolinite is within the range of from 5 : 1 to 1 : 5.

[\*3] 3. A complex consisting essentially of particles of kaolinite coated with a layer-type mineral having the empirical formula:  
 $n\text{SiO}_2:\text{Al}_2\text{O}_3:\text{mAB}:\text{xH}_2\text{O}$

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 2.4 to 3.0,

m is from 0.2 to 0.6,

A is one equivalent of an ...

... [\*3] density than a mechanical mixture of the same said components of said clay-like mineral in said kaolinite.

[\*4] 4. A complex in accordance with claim 3 in which the weight ratio of said layer-type mineral to said kaolinite is within the range of from 5:1 to 1:5.

PAGE 227

LEVEL 1 - 210 OF 225 PATENTS

3,761,171

<=2> GET 1st DRAWING SHEET OF 3

Sep. 25, 1973

NEGATIVE-POSITIVE, POSITIVE-POSITIVE EXPOSURE STATION

INVENTOR: Fields, Gary D., Parker, Colorado

... [\*15] comprising:

means for supporting the photosensitive surface for exposure;

a layered sandwich structure which includes in order:

a first transparent electrode;

a photoconductive layer;

a liquid crystal layer of the type having the capacity to store an image at least temporarily; and

a second transparent electrode;

means for applying a first potential between said electrodes during formation of a temporary image in said ...

... [\*16] means for supporting the charged photoconductive surface for exposure;

a layered sandwich structure which includes in order:

a first transparent electrode;

a photoconductive layer;

a liquid crystal layer of the type having the capacity to store an image at least temporarily; and

a second transparent electrode;

means for applying a first potential between said electrodes during formation of a temporary image in said ...

LEVEL 1 - 211 OF 225 PATENTS

3,720,847

<=2> GET 1st DRAWING SHEET OF 3

Mar. 13, 1973

POWER CURRENT CRYOTRON WITH FLAT GATE CONDUCTOR

INVENTOR: Massar, Ernst, Erlangen, Germany, Federal Republic of

I claim:

[\*1] 1. A power current cryotron comprising an insulating member and a layer type gate conductor superconducting layer on the insulating member, said layer having a thickness in the order of magnitude of the depth of penetration of a magnetic field into the superconducting layer, said insulating member and said layer ...

... [\*1] during operation of said cryotron adjacent portions of said layer conduct current in opposite directions.

[\*2] 2. A power current cryotron comprising a tubular insulating member having an axis and a layer type gate conductor superconducting layer on said insulating member, said layer having a thickness in the order of magnitude of the depth of penetration of a magnetic field into the superconducting layer, said insulating member and said ...

LEVEL 1 - 212 OF 225 PATENTS

3,719,535

<=2> GET 1st DRAWING SHEET OF 1

Mar. 6, 1973

HYPERFINE GEOMETRY DEVICES AND METHOD FOR THEIR FABRICATION

INVENTOR: Zoroglu, Demir S., 4917 North 73rd Street, Apt. 9, Scottsdale, Arizona 85251

... [\*1] sequence of steps and the use of materials for minimizing the number of steps required, comprising the steps of:

providing a semiconductor body of a first type of conductivity and having an upper surface;  
forming a first passivating layer of the type operating to act as a diffusion barrier on said upper surface;

forming a plurality of apertures in said passivating layer which are aligned each to the other;

forming a second passivating layer of the type through which conductivity type determining impurities pass over said first layer and said exposed surface of said semiconductor body;

forming a third passivating layer of the type operating to act as a diffusion barrier over said second layer;

patterning said third layer such as to form at least one aperture overlying a selected aperture in said ...

... [\*6] steps and through the use of materials for minimizing the number of steps required, comprising the steps of:

providing a semiconductor body of a first type of conductivity and having an upper surface;

forming a first passivating layer of the type operating to act as a diffusion barrier on said upper surface;

forming a plurality of apertures in said passivating layer which are aligned each to the other for exposing an equal plurality of surface ...  
E 230

LEVEL 1 - 213 OF 225 PATENTS

3,716,969

<=2> GET 1st DRAWING SHEET OF 2

Feb. 20, 1973

# CONTINUOUS MOVING LAYER TYPE ADSORPTION DEVICE

INVENTOR: Maeda, Isamu, Niihama-shi, Japan

What I claim is:

[\*1] 1. A continuous moving layer type adsorption device employed in a gas desulfurization system, comprising:

a. an adsorption vessel main body filled with activated charcoal, and

b. a rectifying device, said adsorption vessel main ...  
LEVEL 1 - 214 OF 225 PATENTS



Jan. 30, 1973

## MULTI-LAYER COLOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS

INVENTOR: Hayashi, Jun, Kanagawa, Japan  
Sato, Akira, Kanagawa, Japan

What is claimed is:

[\*1] 1. A multi-layer type color photographic light-sensitive material characterized in that a merocyanine dye having the following general formula [I]

wherein X is a member selected from the group consisting of a sulfur atom, a selenium ...

... [\*1] consisting of thiazolines, thiazoles, benzthiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles, benzselenzazoles naphthoselenazoles, benzimidazoles, naphthimidazoles, 2-quinolines, 2-pyridines, and indolines, is incorporated in at least one layer of said multi-layer type color photographic light-sensitive material, said multi-layer type color photographic light-sensitive material comprising, in order,

[\*1] 1. a support,

[\*2] 2. a subbing layer,

[\*3] 3. a red sensitive silver halide emulsion layer,

[\*4] 4. a ...

... [\*5] 1 to 10.0 mole percent, the remaining silver halide emulsion layers containing a silver halide selected from the group consisting of AgBr, AgI, AgCl, AgClBr, AgClI, AgIBr and AgClIBr.

[\*2] 2. The multi-layer type color photographic light-sensitive material as claimed in claim 1 wherein each of R1, R2 and R3 is selected from a group consisting of a hydrogen atom, a methyl group, an ethyl ...

... [\*2] group, a sulfoethyl group, a 4-carboxyphenethyl group, a 4-sulfophenethyl group, a phenyl group, a 4-carboxyphenyl group, and a 4-sulfophenyl group.

Pat. No. 3713828, \*2

[\*3] 3. The multi-layer type color photographic light-sensitive material as claimed in claim 1 wherein the heterocyclic ring completed by Z is selected from the group consisting of the thiazolines, thiazoles, benzthiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles,

benzselenazoles, naphthoselenazoles, indolenines, benzimidazoles, naphthoimidazoles, 2-quinolines and 2-pyridines.

[\*4] 4. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye is incorporated in at least one of the layers consisting of the silver halide emulsion layers and the layers adjacent to the silver halide emulsion layers.

[\*5] 5. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein, after development, cyan, magenta, and yellow images are formed in the red-sensitive, the green-sensitive, and the blue-sensitive silver halide emulsion layers, respectively.

[\*6] 6. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein the silver halide is selected from the group consisting of silver bromide, silver iodide, silver chloride, silver chlorobromide, silver iodobromide, and silver chloro-iodobromide.

[\*7] 7. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye has the formula

[\*8] 8. The multi-layer color photographic light-sensitive material as claimed in ...

PAGE 233

LEVEL 1 - 215 OF 225 PATENTS

3,710,211

<=2> GET 1st DRAWING SHEET OF 1

Jan. 9, 1973

#### FRONT CONTACTED ELECTRICAL COMPONENT

INVENTOR: Behn, Reinhard, Balanstr. 95, Munich, Germany, Federal Republic of  
Gottlob, Heinrich, Annahofstr. 25, Regensburg, Germany, Federal Republic of  
Hoyler, Gerhard, Balanstr. 362, Munich, Germany, Federal Republic of  
Kessler, Hartmut, Dechbettener Str. 19, Regensburg, Germany, Federal Republic of

We claim as our invention:

[\*1] 1. A stacked layer type capacitor for being supported on its lead wires in spaced apart openings on a printed circuit board comprising: a plurality of planar stacked dielectric layers, a metal coating on each of the ...

PAGE 234

LEVEL 1 - 216 OF 225 PATENTS

3,698,296

Oct. 17, 1972

ACTINIC LABEL-MAKING TOOL

INVENTOR: Heuser, Elliott G., Mequon, Wisconsin  
Muttera, Jr., William H., Whitefish Bay, Wisconsin

We claim:

[\*1] 1. A label-making tool adapted for the manufacture of labels from tape which has an adhesive layer and an ultraviolet-imaging layer of the type which activates to visibly change color upon exposure to ultraviolet light and deactivates upon exposure to visible light, said tool comprising, in combination:

I. a housing having a first portion adapted to ...  
LEVEL 1 - 217 OF 225 PATENTS

3,696,499

Oct. 10, 1972

METHOD FOR MAKING A COMPOSITE TUBE

INVENTOR: Dromsky, John A., North Attleboro, Massachusetts

... [\*6] laminate material together.

[\*7] 7. A method for making a double-walled tubing comprising the steps of heating a strip of composite metal laminate material embodying a thin inner layer of Type 304 austenitic stainless steel which is sandwiched between and metallurgically bonded to two relatively thicker outer layers of Type 1008 aluminum-killed low carbon steel to a temperature in the range from about 1850°F. to about 2,005°F. for a period of time in the range from about one-half to 2 minutes, ...

LEVEL 1 - 218 OF 225 PATENTS

3,688,395

Sep. 5, 1972

CONSTRUCTION METHOD OF MAKING ELECTRICAL CONNECTION

INVENTOR: Cummings, Harold K., Whitewater, Wisconsin

... [\*1] contact therewith.

[\*2] 2. The invention in accordance with claim 1,

wherein said base member has an outer conductive surface on which said cutting means is formed, and

wherein said insulated wire is wound to form a coil of the multi-layer type.

[\*3] 3. The invention in accordance with claim 1,

wherein said base member is a terminal to which said insulated wire is to be electrically connected.

[\*4] 4. A method of making a multi-layer electrical ...

37

LEVEL 1 - 219 OF 225 PATENTS

3,664,973

May 23, 1972

HYDROTHERMAL METHOD FOR MANUFACTURING A NOVEL CATALYTIC  
MATERIAL, CATALYSTS CONTAINING SAID MATERIAL, AND PROCESSES  
USING SAID CATALYSTS

INVENTOR: Jaffe, Joseph, Berkeley, California

What is claimed is:

[\*1] 1. A synthetic layer-type, crystalline, clay-like mineral having the empirical formula:

nSiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : mAB : xH<sub>2</sub>O

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 0.4 to 15.0

m is from 0.2 to 0.6

...

... [\*7] hydrogenating component precursor selected from compounds of Group VI metals and compounds of Group VIII metals.

[\*8] 8. A hydrocarbon conversion catalyst cracking component material obtained by the dehydration of a synthetic layer-type, crystalline, clay-like mineral having the empirical formula:

nSiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : mAB : xH<sub>2</sub>O

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 0.4 to 15.0

m is from 0.2 to 0.6

...

... [\*12] a hydrogenating component precursor selected from compounds of Group VI metals and compounds of Group VIII metals.

[\*13] 13. A process of preparing a catalytic component material which comprises dehydrating a synthetic layer-type, clay-like, crystalline mineral having the empirical formula:

nSiO<sub>2</sub> : AL<sub>2</sub>O<sub>3</sub> : mAB : xH<sub>2</sub>O

where the layer lattices comprise said silica, said alumina, and said B, and where Pat. No. 3664973, \*13 PAGE 238

n is from 0.4 to 15.0

m is from 0.2 to 0.6

...

PAGE 239

LEVEL 1 - 220 OF 225 PATENTS

3,626,352

Dec. 7, 1971

#### ATTENUATOR SWITCHES HAVING DEPOSITED LAYER-TYPE CIRCUITRY

INVENTOR: McCoig, Kenneth W., Anaheim, California

... [\*2] said second wafer being movable relative to said first wafer,

an attenuation circuit disposed on a face of said first wafer, said attenuation circuit comprising a resistor array having deposited-layer-type resistors and conductors,

contact means, attached to said first wafer, for making electrical connection to conductors of said resistor array, said contact means having contact ends spring biased against said ...

... [\*2] circuit depending on the relative orientation of said first and second wafers.

[\*3] 3. An attenuator switch as defined in claim 2 wherein said electrically insulative material comprises a ceramic and wherein said deposited layer-type resistors are fabricated of cermet or conductive plastic.

[\*4] 4. An attenuator switch as defined in claim 2 wherein said resistor array comprises first, second, and third resistors connected as a pi ...

... [\*11] spaced parallel relationship with a plurality of rotary wafers, a shaft extending through an opening in the middle of each stationary wafer and cooperating to rotate simultaneously all of said rotary wafers,

a deposited layer-type attenuator section disposed on each of said stationary wafers, each attenuator section comprising deposited layer-type resistors and conductors,

a set of deposited layer-type conductive switch pads disposed on each rotary wafer, and

spring-metal contacts extending from each stationary wafer and electrically connected to the attenuator section thereof, said contacts cooperating with switch pads on an associated rotary wafer to insert or bypass said section depending on the rotational position of said shaft.

[\*12] 12. A step attenuator switch as defined in claim 11 wherein said deposited layer-type attenuator section is disposed on the front face of said stationary wafer and wherein ends of said contacts project rearwardly of said wafer through spaced holes therein.

[\*13] 13. A step attenuator switch as defined in claim 11 wherein said deposited layer-type attenuator section is disposed on the front face of said stationary wafer and wherein ends of said contacts project forwardly of said wafer.

Pat. No. 3626352, \*13

PAGE 240

[\*14] 14. A step attenuator switch as defined in claim 11 wherein ...

... [\*14] each contact being attached by a fastener spaced a selected distance from a free end of said each contact,

said attenuator section comprising first, second, and third deposited layer-type resistors connected in pi configuration, a first deposited layer-type conductor connecting the junction of said first and second resistors to one of said contacts, a second deposited layer-type conductor connecting the junction of said second and third resistors to a second of said contacts, the junction of said first and third resistors being connected to a common terminal by a third deposited layer-type conductor, and

a pair of input/output terminals electrically connected respectively to said third and said fourth contacts.

[\*15] 15. A bridged-T attenuator comprising:

a wafer of electrically insulative material,

portions of a bridged-T circuit disposed on both major faces of said wafer and formed of deposited layer-type components, and

wiper contact means rotatable with respect to said wafer and cooperating with said deposited layer-type components for controlling the attenuation of said attenuator.

[\*16] 16. A bridged-T attenuator as defined in claim 15 wherein said wafer comprises a refractory material and has a central opening ...

... [\*16] being attached to a shaft extending through said opening, said attenuator further comprising an input terminal, an output terminal and a common terminal all attached to said wafer, a pair of deposited layer-type fixed resistors being connected in series by means of deposited layer-type conductors between said input and output terminals.

[\*17] 17. A bridged-T attenuator as defined in claim 16 further comprising: a first annular deposited layer-type conductive switch pad disposed on one major face of said wafer surrounding said opening and electrically connected by means of a deposited layer-type conductive strip to said input terminal,

a first plurality of deposited layer-type conductive switch pads disposed in a circle on said one major face surrounding said central opening, a pair of said first plurality of switch pads being electrically connected respectively to said input and output terminals, and

a first plurality of deposited layer-type relative elements disposed on said one major face and electrically connected between adjacent ones of said first plurality of switch pads, said wiper contact means selectively electrically shorting one of ...

... [\*17] controlling the effective resistance of one portion of said bridged-T circuit.

Pat. No. 3626352, \*17

PAGE 241

[\*18] 18. A bridged-T attenuator as defined in claim 17 further comprising:

a second annular deposited layer-type conductive switch pad disposed on the other major face of said wafer surrounding said opening and electrically connected by means of a deposited layer-type conductive strip to the junction of said pair of fixed resistors,

a second plurality of deposited layer-type conductive switch pads disposed in a circle on said other major face surrounding said central opening

a second plurality of deposited layer-type resistive elements disposed on said other major face, one of said second plurality of resistive elements being electrically connected between one of said second plurality of switch pads and said common ...

LEVEL 1 - 221 OF 225 PATENTS

3,617,491

Nov. 2, 1971

PAGE 242

HYDROCRACKING CATALYST COMPRISING A LAYERED CLAY-TYPE  
CRYSTALLINE ALUMINOSILICATE COMPONENT, A GROUP VIII

COMPONENT AND A THORIUM OR URANIUM COMPONENT, AND PROCESS  
USING SAID CATALYST

INVENTOR: Csicsery, Sigmund M., Lafayette, California

... [\*5] metals, and wherein said hydrogenating components are contained in said matrix.

[\*6] 6. A catalyst as in claim 5, which further comprises Titania.

[\*7] 7. A catalyst comprising:

A. A dehydrated layer-type, crystalline, claylike mineral-cracking component which prior to dehydration has the empirical formula  $n\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{mAB} : x\text{H}_2\text{O}$ ,

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 2.4 to ...

LEVEL 1 - 222 OF 225 PATENTS

3,617,490

Nov. 2, 1971

PAGE 243

HYDROCRACKING CATALYST COMPRISING A LAYERED CLAY-TYPE  
CRYSTALLINE ALUMINOSILICATE COMPONENT, A GROUP VIII  
COMPONENT, AND A CHROMIUM OR TUNGSTEN COMPONENT, AND PROCESS  
USING SAID CATALYST

INVENTOR: Csicsery, Sigmund M., Lafayette, California

... [\*5] metals, and wherein said hydrogenating components are contained in said matrix.

[\*6] 6. A catalyst as in claim 5, which further comprises titania.

[\*7] 7. A catalyst comprising:

A. A dehydrated layer-type, crystalline, claylike mineral cracking component which prior to dehydration has the empirical formula  $n\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{mAB} : x\text{H}_2\text{O}$ ,

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 2.4 to 3.0

...

LEVEL 1 - 223 OF 225 PATENTS

PAGE 244



Nov. 2, 1971

HYDROCRACKING CATALYST COMPRISING A LAYERED CLAY-TYPE  
CRYSTALLINE ALUMINOSILICATE COMPONENT, A GROUP VIII  
COMPONENT AND GOLD, PROCESS USING SAID CATALYST

INVENTOR: Csicsery, Sigmund M., Lafayette, California

... [\*6] metals, and wherein said hydrogenating components are contained in said matrix.

[\*7] 7. A catalyst as in claim 6, which further comprises titania.

[\*8] 8. A catalyst comprising:

A. a dehydrated layer-type, crystalline, claylike mineral cracking component which prior to dehydration has the empirical formula

$n\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{mAB} : x\text{H}_2\text{O}$ ,

where the layer lattices comprise said silica, said alumina, and said B, and where

n is from 2.4 to 3.0

...

LEVEL 1 - 224 OF 225 PATENTS

PAGE 245

Oct. 26, 1971

COLOR PHOTOGRAPHIC DEVELOPING PROCESS

INVENTOR: Ohi, Reiichi, Kanagawa, Japan  
Shimamura, Isao, Kanagawa, Japan  
Shishido, Tadao, Kanagawa, Japan

... [\*4] black and white developer or in a pretreatment bath before the black and white development.

[\*5] 5. The process according to claim 1 wherein said multilayer color photographic element is a coupler-in-emulsion layer-type color photographic element and said compound is incorporated in the black and white developer.

[\*6] 6. The process according to claim 1 wherein said process is a high temperature process conducted at a temperature higher than ...

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LEVEL 1 - 225 OF 225 PATENTS

PAGE

3,611,078

Oct. 5, 1971

# STABILIZED AC SUPERCONDUCTOR

INVENTOR: Massar, Ernst, Erlangen, Germany, Federal Republic of  
Parsch, Claus-Peter, Erlangen, Germany, Federal Republic of

We claim:

[\*1] 1. An AC superconductor, comprised of a superconducting layer of type I intended for the load current, which is placed with a minimum contact resistance upon a metallic stabilizing layer of a superconducting material of type III, which during overloading absorbs the current, at least partially and temporarily, said superconductor of type I encloses said superconductor of type III provided for stabilizing purposes in the form of a tube.

[\*2] 2. The superconductor of claim 1 wherein the superconducting layer of type I is lead.

[\*3] 3. The superconductor of claim 1, wherein the superconductors are concentric tubes.

[\*4] 4. The superconductor of claim 3, wherein at least two mutually contacting layers of superconducting material of type III, provided for stabilization, are ...

... [\*7] tube upon whose outer wall the superconductor layers are placed.

[\*8] 8. The superconductor of claim 5, wherein the thickness of the respective superconducting layer is between 1 and 10  $\mu$ .

[\*9] 9. An AC superconductor, comprised of a superconducting layer of type II intended for the load current, which is placed with a minimum contact resistance upon a metallic stabilizing layer of a superconducting material of type III, which during overloading absorbs the current at least ...

... [\*11] III, provided for stabilization, are present which have higher critical field strengths for the alternating current the further they are from the superconductor of type II which is provided for the current load.

[\*12] 12. The superconductor of claim 9 wherein the superconducting layer of type II is niobium.

\* 246 PAGES 4940 LINES JOB 68990 1006J \*  
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PAGE 1

FOCUS - 1 OF 5 PATENTS

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MESSAGE: Attached is a copy of the Affidavit of  
Thomas Shaw under 37CFR 1.132 Submitted on 12/15/98

Dan Morris

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

AFFIDAVIT UNDER 37 CFR 1.132

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y.

from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications. I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.



3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.

4) Thermal Behaviour of Compositions in the Systems  $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Thomas M. Shaw  
Thomas M. Shaw

Sworn to before me this 14<sup>th</sup> day of December, 1998.

Sandra M. Emma  
Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

Filing: Affidavit Under 37 CFR 1.132 of Peter R. Duncombe, Attachment A (Resume); Filing: Affidavit Under 37 CFR 1.132 of Peter R. Duncombe, Attachment A (Resume), Attachment B (Book IV), Attachment C (Book V), Amendment After Final Rejection Under 37 CFR 1.116

PLMAS

in re application of:

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For: NEW SUPERCONDUCT

in re application of: J. Bednorz et al.

Serial No. 08/303,561;

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION

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Serial No. 08/303,561; Decret, No. 7Y0987-074BY Atty.: DPM

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 18, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

In the referenced final Office Action, the Examiner refers to three affidavits (of Mitzi, Tsuei and Dinger) submitted by applicants to overcome the rejection under 35 USC 112 for a lack of enablement. The Examiner's comments are at (paragraph (d)(iv) page 7, 5 lines from the bottom to page 8, 4 lines from the bottom. The Examiner states:

(d)(iv)(1) "Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make these superconductors without undue experimentation."

(d)(iv)(2) "Those affidavits do not overcome the non-enablement rejection."

(d)(iv)(3) "Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made."

Moreover, in applicant's response dated May 14, 1998, applicants refer to Poole et al. which states at page 59 thereof "[c]opper oxide superconductors with a parity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials" (see applicant's response for the entire text that is quoted and Attachment A thereof for copies of relevant pages from Pool et al.)

In response the Examiner states:

(1) Initially, however, it should be noted that the Poole article was published *after* the priority date presently claimed. As such, it does not provide evidence of the state of the art *at the time* the presently claimed invention was made.

(2) Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting condition.

Applicants respectfully disagree with the Examiner. In further support of applicants position that all their claims are fully enabled, applicant's submit herewith the affidavit under 37 CFR 1.132 of Peter Duncombe which provides a list of books and articles published prior to applicants filing date showing the general principles of ceramic science used by applicants and which are used as stated by Poole et al. to make the

high Tc superconductors taught and claimed by applicants which "are not difficult to synthesize."

The affidavit of Peter Duncombe provides complete copies of two of his notebooks in which he sets forth particular facts in which he recorded the synthesis and properties of high Tc superconducting materials fabricated according to the general principles of ceramic science as taught by applicants.

Applicants submitted by facsimile an affidavit of James W. Leonard on December 15, 1998 which states that 5,689 articles cited the applicants' Zeitschrift fur Physik B-Condensed Matter, **64**, pp. 189-193 (Sept. 1986) article. It cost \$2.50 per citation to print each citation for a total cost of \$14,222.50. Applicants will supply this list at the USPTO's request.

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

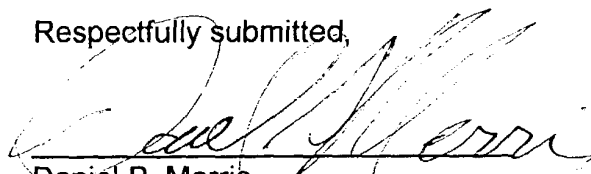
If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,

A handwritten signature in dark ink, appearing to read "Daniel P. Morris", is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 18, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AFFIDAVIT UNDER 37 CFR 1.132**

Sir:

I, Peter R. Duncombe, being duly sworn, do hereby depose and state:

I received a B.A. degree in Chemistry from the State University of New York at New Paltz, New Paltz, N.Y. and a M.S. degree in Chemical Engineering (1983) from the State University of New York at Buffalo, Buffalo, N.Y.

I have worked as a graduate research assistant in the Chemical Engineering Department of SUNY at Buffalo from 1980-1983. I have worked as a chemical engineer in Ceramics Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, N.Y. from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications (Attachment A).

I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the



work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-181, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., *Revue de Chemie minerale*, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$ , V.S. Chincholkar et al. *Therm. Anal.* 6th, Vol. 2., p. 251-6, 1980.

I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1988 and in technical notebook V with entries continuing from June 7, 1988 to May 2, 1989. Complete copies of each of these notebooks are attached - Attachment B - Book IV and Attachment C - Book V. Below is a listing of some of the compounds I prepared and recorded in these notebooks according to the teaching as described in the Bednorz and Mueller patent application using the general principles of ceramic science as described in the books and articles listed above.

In Book IV,  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$  batch C1 pellet pressing, sintering notes and powder processing specifications start on page 2 and continue intermittently to pg. 40 (pg. 13 has superconductive susceptibility curves for pellet 9). Batch C2  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_3$  detailed from pages 14 to 47.

In Book V green phase ( $\text{Y}_2\text{BaCuO}_x$ ) microstructural photomicrographs are logged on pages 15-17 with notes continuing to pg. 19. The perovskite superconductor  $\text{BiSrCaCu}$  oxide ( $\text{Bi}_{2.15}\text{Sr}_{1.68}\text{Ca}_{1.7}\text{Cu}_2\text{O}_{8+\delta}$ ) and related perovskites  $\text{Ca}_{(2-x)}\text{Sr}_x\text{CuO}_x$  and  $\text{Bi}_2\text{Sr}_2\text{CuO}_x$  synthesis notations start and continue through pg. 61 with microstructural photomicrographs.

A series of  $Y_1Ba_2Cu_3O_x$  stoichiometric perturbations to study compositional effects on 2nd phase or grain boundary phases and their effect on conductivity (resistivity), sintering behavior etc., continue until the end of the book notes on the page dated May 2, 1989 (page not numbered). These are typical perovskite synthetic procedures, microstructural photomicrographs, powder processing methods, characteristic susceptibility curve(s), sintering behavior and the like. Additional notes may be available in later notebooks.

The undersigned affiant swears further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or patent issuing thereon.

By: Peter R. Duncombe  
Peter R. Duncombe

Sworn to before me this 18<sup>th</sup> day of December, 1998.

Sandra M. Emma  
Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

## ATTACHMENT A

# RESUME 1998

1. Compensation doping of Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> thin films  
Copel, M Baniecki, JD Duncombe, PR Kotecki, D  
Laibowitz, R Neumayer, DA Shaw, TM  
APPLIED PHYSICS LETTERS V73 N13 SEP 28 1998 P1832-1834
2. Method for Forming Noble Metal Oxides and Structures Formed Thereof. June 1998.  
Duncombe, P. R. Hummel, J. P. Laibowitz, R. B.  
Neumayer, D. A. Saenger, K. L. Schrott, A. G.  
RC 98A 41575
3. Growth of Bismuth Titanate Films By Chemical Vapor Deposition and Chemical Solution  
Deposition. March 1998. RC-21124  
Neumayer, D. A. Duncombe, P. R. Laibowitz, R. B.  
Shaw, T. Purtell, R. Grill, A.
4. Dielectric relaxation of Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> thin films from 1 mHz to 20 GHz Baniecki, JD  
Laibowitz, RB Shaw, TM Duncombe, PR  
Neumayer, DA Kotecki, DE Shen, H Ma, QY  
APPLIED PHYSICS LETTERS V72 N4 JAN 26 1998 P498-500
5. Contrasting magnetic and structural properties of two La manganites with the same  
doping levels  
McGuire, T.R. Duncombe, P.R. Gong, G.Q. Gupta, A. Li, X.W. Pickart, S.J. Crow, M.L.  
J. Appl. Phys. (USA) Vol.83, No.11 1 June 1998 P7076-8
6. Effects of Annealing Conditions on Charge Loss Mechanisms in MOCVD (Ba<sub>0.7</sub>,Sr<sub>0.3</sub>)TiO<sub>3</sub>  
Thin Film Capacitors.  
Baniecki, J.D., Laibowitz, RB Shaw, TM Duncombe, PR Saenger, KL Cabral C  
Kotecki, DE , Shen, H, Lian, J., Ma, QY
7. Low Operating Voltage and High Mobility Field Effect Transistors Comproising Pentacene  
and Relatively High Dielectric Constant Insulators RC21233(94806) 7/17/98  
Dimitrakopoulos, CD Purushothaman S, Kymissis J. Callegari A. , Neumayer DA,  
Duncombe PR, Laibowitz RB, Shaw JM
8. Maximum Magnetoresistance in Granular Manganite/Insulator System close to Percolation  
Threshold PACS 10/06/98  
DK Petrov, L Krusin-Elbaum, JZ Sun, C Feild, & PR Duncombe
9. Magnetoresistance and Hall Effect of Chromium Dioxide Epitaxial Thin Films  
X.W. Li, A. Gupta, T.R. McGuire, P.R. Duncombe, Gang Xiao
10. Progress Report on High-k dielectric material: amorphous BST from solgel (09/98)  
P. Andry, D. Neumayer, P. Duncombe, C. Dimitrakopoulos, F. Libsch, A. Grill, R. Wisnieff

RC21352(96175)2 Dec 1998

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INCOMPLETE

## Personal Inventor History

Name: Duncombe, P.R.      Serial: 155139      Loc: RES YORKTOWN  
Patent Pts: 36      TDB Pts: 1      Total Pts: 37      Plateau Lvl: 3  
Plateau Date: 10/24/98      File Update: 11/02/98  
Awards Due: None

Title: NOVEL METAL ALKOXYALKOXIDECARBOXYLATES AND USE TO FORM FILMS

06/17/98 Opened as Discl YO8980231      Status: Filed

06/22/98 Discl Review      Action: File

① 09/04/98 Filed as Docket YO998254 in US      Rating: 2      Pts: 3  
Co-inventors: Neumayer, D.A.

Title: SELECTIVE GROWTH OF FERROMAGNETIC FILMS FOR MAGNETIC MEMORY, STORAGE-BASED DEVICES, AND OTHER DEVICES

06/17/98 Opened as Discl YO8980225      Status: Filed

06/29/98 Discl Review      Action: File

④ 10/15/98 Filed as Docket YO998268 in US      Rating: 2      Pts: 3  
Co-inventors: Guha, S. Gupta, A. Bojarczuk, N.A. Karasinski, J.M.

Title: BEOL DECOUPLING CAPACITOR MATERIALS

01/28/98 Opened as Discl YO8980024 in US      Status: Opened

06/24/98 Discl Review      Action: File

Co-inventors: Rosenberg, R. Ning, T.H. Shaw, T.M. Edelstein, D.C. Neumayer, D.A. Laibowitz, R.B.

③ "FABRICATION OF Strontium Bismuth Titanate/Bismuth Titanate Multilayer Ferroelectric"  
Title: FERROELECTRIC THIN FILM STRUCTURES

10/01/97 Opened as Discl YO8970512 in US      Status: Opened

09/16/98 Discl Review      Action: File

② 10/30/98 SENT TO COUNSEL (L. Schwes)      Co-inventors: Shaw, T.M. Neumayer, D.A. Laibowitz, R.B.

Title: CAPACITORS WITH AMORPHOUS DIELECTRICS AND IMPROVED DIELECTRIC PROPERTIES MADE USING SILICON SURFACES AS ELECTRODES

06/06/97 Opened as Discl YO8970261 in US      Status: Opened

Co-inventors: Shaw, T.M. Neumayer, D.A. Laibowitz, R.B.

Title: FABRICATION OF THIN FILM FIELD EFFECT TRANSISTOR COMPRISING AN ORGANIC SEMICONDUCTOR AND CHEMICAL SOLUTION DEPOSITED METAL OXIDE

03/25/97 Opened as Discl YO8970113      Status: Filed

03/25/97 Discl Review      Action: File

03/25/97 Filed as Docket YO997083 in US      Rating: 2      Pts: 3

03/24/98 Filed as Docket YO997083 in JA      Rating: 2

⑥ 03/16/98 Filed as Docket YO997083 in TA      Rating: 2

03/12/98 Filed as Docket YO997083 in KO      Rating: 2

04/24/98 Last Office Action

Co-inventors: Purushothaman, S. Dimitrakopoulos, C.D. Furman, B.K. Neumayer, D.A. Laibowitz, R.B.

Title: NOVEL ALKOXYALKOXIDES AND USE TO FORM FILMS

10/30/96 Opened as Discl YO8960411      Status: Filed

03/10/97 Discl Review      Action: File

⑤ 01/30/98 Filed as Docket YO997069 in US      Rating: 2      Pts: 3  
Co-inventors: Neumayer, D.A.

Title: THIN-FILM FIELD-EFFECT TRANSISTOR WITH ORGANIC SEMICONDUCTOR REQUIRING LOW OPERATING VOLTAGES

09/11/96 Opened as Discl YO8960358

Status:Filed

03/04/97 Discl Review

Action:File

⑦ 03/25/97 Filed as Docket YO997057 in US

Rating: 2

Pts:3

03/12/98 Filed as Docket YO997057 in KO.

Rating: 2

04/10/98 Last Office Action

Co-inventors: Purushothaman, S. Dimitrakopoulos, C.D. Furman, B.K. Neumayer, D.A. Laibowitz, R.B.

X Title: HIGH DIELECTRIC CONSTANT, BARIUM LANTHANUM TITANATE THIN FILM CAPACITORS FOR RANDOM ACCESS

06/20/96 Opened as Discl YO8960255 in US

Status:Opened

Co-inventors: Gupta, A. Shaw, T.M. Laibowitz, R.B.

Title: METHOD FOR FORMING NOBLE METAL OXIDES AND STRUCTURES FORMED THEREOF

10/30/95 Opened as Discl YO8950450

Status:Filed

11/12/96 Discl Review

Action:File

11/05/97 Filed as Docket YO996239 in US

Rating: 2

Pts:3

⑧ 10/20/98 Filed as Docket YO996239 in JA

Rating: 2

07/30/98 Filed as Docket YO996239 in TA

Rating: 2

Co-inventors: Schrott, A.G. Saenger, K.L. Hummel, J.P. Neumayer, D.A. Laibowitz, R.B.

Title: PEROXIDE ETCHANT PROCESS FOR PEROVSKITE-TYPE OXIDES

10/23/95 Opened as Discl YO8950434

Status:Filed

08/08/97 Discl Review

Action:File

⑨ 04/08/98 Filed as Docket YO997256 in US

Rating: 2

Pts:3

Co-inventors: Rosenberg, R. Cooper, E.I. Laibowitz, R.B.

Title: RF TRANSPONDER FOR METALLIC SURFACES

08/02/95 Opened as Discl YO8950329 in US

Status:Opened

Co-inventors: Afzali-ardakani, A. Feild, C.A. Duan, D.W. Brady, M.J. Moskowitz, P.A.

Title: METHOD FOR CLEANING THE SURFACE OF A DIELETRIC

09/06/95 Opened as Discl FI8950292

Status:Filed

09/06/95 Sent to Evaluator

02/05/96 Evaluated

Action:Search

04/19/96 Discl Review

Action:File

12/06/96 Filed as Docket FI996047 in US

Rating: 2

Pts:3

11/29/97 Filed as Docket FI996047 in KO

Rating: 2

05/26/97 Filed as Docket FI996047 in TA

Rating: 2

06/11/98 Last Office Action

Co-inventors: Kotecki, D.E. Wildman, H.S. Yu, C. Natzle, W. Laibowitz, R.B.

Title: NANO PHASE FABRICATION OF COPPER-GLASS CERAMIC COMPOSITE VIAS IN CORDIERITE SUBSTRATES

10/05/92 Opened as Discl YO8920907 in US

Status:Published

10/08/92 Sent to Evaluator

12/17/92 Discl Review

Action:Publish

01/06/93 Mailed to Tech Discl Bulletin

09/02/93 Published

Pts:1

Co-inventors: Kang, S.K. Shaw, T.M. Brady, M.J.

Title: METHOD OF SINTERING ALUMINUM NITRODE

11/06/92 Opened as Discl FI8920668 in US

Status:Closed

11/06/92 Sent to Evaluator

12/18/92 Closed

Co-inventors: Takamori, T. Shinde, S.L.

Title: METHOD OF SINTERING ALUMINUM NITRIDE

11/06/92 Opened as Discl FI8920667 in US Status:Closed  
11/06/92 Sent to Evaluator  
12/18/92 Closed  
Co-inventors: Takamori, T. Shinde, S.L.

Title: ALUMINUM NITRIDE BODY AND METHOD FOR FORMING SAID BODY UTILIZING A VITREOUS SINTERING ADDITIVE

08/13/92 Opened as Discl FI8920525 Status:Filed  
08/17/92 Sent to Evaluator  
09/29/92 Evaluated Action:Search  
12/23/92 Discl Review Action:File  
05/10/95 Filed as Docket FI992168B in US Rating: 2 Pts:3  
05/28/96 Issued as Patent 5520878 in US  
Co-inventors: Takamori, T. Shinde, S.L.

Title: ALUMINUM NITRIDE BODY AND METHOD FOR FORMING SAID BODY UTILIZING A VITREOUS SINTERING ADDITIVE

08/13/92 Opened as Discl FI8920525 Status:Filed  
08/17/92 Sent to Evaluator  
09/29/92 Evaluated Action:Search  
12/23/92 Discl Review Action:File  
12/22/93 Filed as Docket FI992168A in US Rating: 2 Pts:3  
01/09/96 Issued as Patent 5482903 in US  
Co-inventors: Takamori, T. Shinde, S.L.

Title: GOLD DOPING OF YBA2CU3O7-8 AS A MEANS OF INCREASING TRANSPORT CRITICAL CURRENT DENSITY

02/12/92 Opened as Discl YO8920161 in US Status:Closed  
02/14/92 Sent to Evaluator  
05/15/92 Closed  
Co-inventors: Daeumling, M. Shaw, T.M.

Title: PROCESS FOR PRODUCING CERAMIC CIRCUIT STRUCTURES HAVING CONDUCTIVE VIAS

07/19/89 Opened as Discl YO8890552 Status:Filed  
07/25/89 Sent to Evaluator  
08/10/89 Evaluated Action:Search  
07/30/90 Discl Review Action:File  
12/17/92 Filed as Docket YO990091B in US Rating: 2 Pts:3  
08/16/94 Issued as Patent 5337475 in US  
Co-inventors: Vallabhaneni, R.V. Giess, E.A. Farooq, S. Cooper, E.I. Kim, Y.H. Vanhise, J.A. Aoude, F.Y. Muller-landau, F. Shaw, R.R. Walker, G.F. Rita, R.A. Neisser, M.O. Park, J.M. Shaw, T.M. Brownlow, J.M. Kim, J. Knickerbocker, S.H.

Title: VIA PASTE COMPOSITIONS AND USE THEREOF TO FORM CONDUCTIVE VIAS IN CIRCUITIZED CERAMIC SUBSTRATES

07/19/89 Opened as Discl YO8890552 Status:Filed  
07/25/89 Sent to Evaluator  
08/10/89 Evaluated Action:Search  
07/30/90 Discl Review Action:File  
03/20/91 Filed as Docket YO990091A in US Rating: 2 Pts:3  
02/01/94 Issued as Patent 5283104 in US  
Co-inventors: Vallabhaneni, R.V. Giess, E.A. Farooq, S. Cooper, E.I. Kim, Y.H. Vanhise, J.A. Aoude, F.Y. Muller-landau, F. Shaw, R.R. Walker, G.F. Rita, R.A. Neisser, M.O. Park, J.M. Shaw, T.M. Brownlow, J.M. Kim, J. Knickerbocker, S.H.

Call your award coordinator, IPL department, or T/L 826-2680 for help.

**SEND****MAIN  
MENU****OTHER  
OPTIONS**



NAME: Duncombe Peter REmp. Ser: 155139Date: 10/23/95

- T.R. McGuire, A. Gupta, P.R. Duncombe, M. Rupp, J.Z. Sun, R.B. Laibowitz, W.J. Gallagher & G. Xiao "Magnetoresistance and Magnetic Properties of  $(La_{1-x})MnO_{3-\delta}$  Thin Films" 3M Conf. Proc: 4/96
- T.R. McGuire, P.R. Duncombe, G.Q. Gong, A. Gupta, X.W. Li & G. Xiao "Magnetoresistance & Magnetic Properties of  $(La_{1-x})MnO_{3-\delta}$  (Vacancy) Bulk Materials" 11/96 3M conf CMR Open Forum entry
- J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P.R. Duncombe, W.J. Gallagher & S. P. Parkin "Magneto-Transport in Doped Manganate Perovskites" 3M conference 11/12-15/96 Atlanta, Georgia
- P. Lecoeur, A. Gupta, P.R. Duncombe, G. Gong & G. Xiao "Emission Studies of the Gas-Phase Oxidation of Mn during Pulsed Laser Deposition Manganates in O<sub>2</sub> & N<sub>2</sub>O Atmospheres" JAP 80(1), 7/1/96
- J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P.R. Duncombe, W.J. Gallagher & S.S.P. Parkin "Colossal Magnetoresistance in Doped Manganate Perovskites" IBM J&D to appear 1996/97
- A. Gupta, G.Q. Gong, G. Xiao, P.R. Duncombe, P. Trouilloud, P. Lecoeur, Y.Y. Wang, V.P. Dravid, & J.Z. Sun "Grain Boundary Effects on the Magnetoresistance Properties of Perovskite Manganite Films"
- J.Z. Sun, W.J. Gallagher, P.R. Duncombe, L. Krusin-Elbaum, R.A. Altman, A. Gupta, Y. Lu, G.Q. Gong & G. Xiao "Observation of Large Low-field Magnetoresistance in Tri-layer Perpendicular Transport Devices Made Using Doped Manganate Perovskites" to appear Appl. Phys. Lett.
- J.Z. Sun, L. Krusin-Elbaum, P.R. Duncombe, A. Gupta & R. B. Laibowitz "Spin-Polarized Tunneling in Doped Perovskite Manganate Trilayer Junctions" APL submission 11/96
- T.R. McGuire, P.R. Duncombe, C.Q. Gong, A. Gupta, X.W. Li & G. Xiao "Interlayer Exchange Coupling & Magnetoresistance Of LCMO/LSMO 67/33 Multilayers" APL submission
- R.B. Laibowitz, T.M. Shaw, D.E. Kotecki, S. Tiwari, A. Gupta, A. Grill, & P.R. Duncombe "Properties and Applications of Thin Films of Lead Lanthanum Titanate (PLT) and Barium Strontium Titanate (BST) APS mtg 3/18-22/96
- P.R. Duncombe, S.L. Shinde, & T. Takamori "Aluminum Nitride Body Utilizing A Vitreous Sintering Additive" US05482903 1/9/96 (EF Plaque)
- P.R. Duncombe, S.L. Shinde, & T. Takamori "Aluminum Nitride Body & Method for Forming Said Body Utilizing a Vitreous Sintering Additive" US05520878 issued 5/28/96; I.A. Patent issue Award: 8/96
- Ali Afzali-Ardakani, Mike Brady, Dah-Wei Duan, Peter Duncombe, Chris Feild, and Paul Moskowitz "RF Transponder for Metallic Surfaces" Docket#:YO895-0329 submitted: 8/2/95
- D.E. Kotecki, R.B. Laibowitz, W. Natze, C. Yu, H. Wildman, P.R. Duncombe "Method for Cleaning the Surface of BST Prior to Electrode Deposition" Application #:FI996047 draft #1 under review
- E.I. Cooper, P.R. Duncombe, R.B. Laibowitz, "Peroxide Etchant Process for Titanate Dielectrics" Docket: YO895-0434 rated file; in prep.
- D.A. Neumayer, P.R. Duncombe, R.B. Laibowitz, & A. Grill "Sol-Gel Processing of BaSrTiO<sub>3</sub> Films" submitted to International Symposium on Integrated Ferroelectrics (ISIF: 3/2-5/97) Santa Fe, N.M.
- A. Grill, R. Laibowitz, D. Beach, D. Neumayer & P.R. Duncombe "Effect of Base Electrode on the Crystallization & Electrical Properties of PLT" IBM RC 20402 (90185) 3/5/96
- D.A. Neumayer, P.R. Duncombe, R.B. Laibowitz & A. Grill "Effect of TiO<sub>x</sub> Nucleation Layer on Crystallization of Sol-Gel Derived Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> Films" ISIF submission 3/97
- C.D. Dimitrakopoulos, P.R. Duncombe, B.K. Furman, R.B. Laibowitz, D. Neumayer, S. Purushothaman, J. Shaw "Field Effect Transistor for Low Voltage Operation" Disclosure YO896-0358 rated file: 9/11/96
- R.B. Laibowitz, P.R. Duncombe, D. Neumayer, K.L. Saenger, A.G. Schrott "Noble Metal Surfaces" YO896-04xx rated "file" 10/96
- T. Shaw, R.B. Laibowitz, P.R. Duncombe & A. Gupta "High Dielectric Constant Barium Lanthanum Titanate-Based DRAM Structures" Disclosure #: YO898-0681 rated File 5/96 in preparation
- D. Neumayer, P.R. Duncombe "Fabrication of Barium Strontium Titanate Films" YO896-04xx rated File 10/96 in preparation

IBM Commitments:

To Win

To Execute

To Teamwork



ATTACHMENT B

401001

Technical Notebook

Book IV

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P DUNCOMBE

Employee Serial:

156139

Date of First Entry:

Date of Last Entry:

Security Classification:

11/12/87

6/88

MORAR

1

11/12

IBM Technical Notebook

70/30 - 25-25 } CLCEP2 - ~ 12:30 start

3.094 0.574 0.179 4.07  
1.458 0.455 0.760

"63.9" 123 basis  
84.6!?

~ 4 hrs

3.047 0.515 0.158 5.65  
≤ ~ 1.5% loss 1.308 0.401 0.539

88.7 better  
P1 → 83.4

11/12

11/13 SrTiO<sub>3</sub> - ST3 → 32 hrs ST2 pos. → 48

SrTiO<sub>3</sub> ⇒ ST3 → cooked in morning see book III, pg (A7)

4.024 0.510 ✓ 0.240 ✓ ~ 5.01 "1.04(2)% dense"  
no wgt loss 1.295 0.610 0.803 same Sally

~ 48 hrs (+ cooling 3 mornings, stepwise) sintering pellet

Cutting record

start 0.425 (0)  
+ 0.060 Δ - saw (0.015) = 0.045 ~ 1.14 mm w/ flattening ~ 1 mm ✓  
0.485 (Δ 0) ↳ 0.042 (1.08 mm) OK

0.060  
0.545 (0.045 Δ resid; actual ⇒ 0.052 → 1.32 mm)

(55)

0.0465 1.18 mm

0.0523

bottom (0.6 - 0.69) not flat 1.52 mm

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Date and sign entry. Have every possibly important entry witness submit an Invention Disclosure of anything possible, new and inventive.

10/13  
2

# IBM Technical Notebook

PRE  
 STA - some deformity on 1 side (a slice worth)  
 4.178 0.584 ~0.287 3.316  
 1.483 0.729 1.26  
 May final piece of ST2 @ 4.55  
 68.9  
 average

will remove Monday morn: ~ 6-6 SAT, 6 SAT-6 SUN, ~ 63<sup>+</sup> hours projected

10/16  
 4.169 0.510 ~0.250 4.98 1.035 <CONSISTENT>  
 (0.2%) 1.295 0.635 0.837

G1 ISO-26,000 UCL-3300  
 4.01 0.578 0.248 0.542 3.76  
 1.468 0.630  
 1.066

density est. (figure 65%) => 5.785 RANGE (5.37-6.27)

C1Z51  
 10/17 3300 / 26,000 EXTREMELY SHINY, flat surface, all corners sharp curved pellet  
 3.105 0.566 0.193(4) 3.90 61.2%  
 1.438 0.490 0.796

G1 16 hrs  
 3.985 0.578 0.250 (no change) 3.738 (lost 0.5% density)

10:18 in hot furnace, packed T<sub>c</sub> - 520C  

|      | T <sub>c</sub> | T <sub>s</sub> | T <sub>SET</sub> |   |
|------|----------------|----------------|------------------|---|
| 20   | 977            | 745            | 971              | to 'push' ΔT                              |
| 21   | ↓              | 838            |                  |   |
| 22   |                | 898            |                  |   |
| 23   |                | 935            |                  | 23 1/2 → 951                              |
| 24   |                | 949            | 956              | ~ SET-PT.                                 |
| 2:23 |                |                |                  | "OFF" for slo-cool (first stepped to 840) |
| 2:54 | 435            |                |                  |   |

Date and sign every entry. Have every entry witnessed. Submit an Invention Certificate if important and new and inventive.

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3

10/17

C12F1  $\Rightarrow$  pellet multiply cracked as if organic residue vaporized, evidence of vapor transport to support plate, etc. ~~ex~~ Not

2.925  $\Delta$  0.18  
 (5.5%)

9.79 - 3.105  $\Rightarrow$  6.685

10/18

G1 - post 4.044 split in 4 pieces (seemingly on cooling)

|        |       |       |       |                                       |
|--------|-------|-------|-------|---------------------------------------|
| G2 4.1 | 0.579 | 0.253 | 3.75  | ✓ pellet slightly disfigured, but ok. |
|        | 1.471 | 0.643 | 1.093 |                                       |

33

|  |       |       |       |                        |
|--|-------|-------|-------|------------------------|
|  | 4.155 |       |       |                        |
|  | 0.510 | 0.220 | 5.64  | about expected density |
|  | 1.295 | 0.559 | 0.736 |                        |

D.D.1 Pre  
 3.10

0.5765" 0.191"

3.14

|       |       |       |      |
|-------|-------|-------|------|
| 0.513 | 0.165 | 5.61  | 88.2 |
| 1.303 | 0.419 | 0.559 |      |

The above understood and witnessed by

Date

and  
by

Date

575

4  
11/24

IBM Technical Notebook

Thermodyne Tube furnace set-up specs.

thermocouple: dia. ~0.255 length 20" + USED 23"

Set-up complete w/ plug in jacks, ext. wire, 5 couples.

11/30 Analytical Submissions

|             |                             |                 |
|-------------|-----------------------------|-----------------|
| C1 - 0.75 g | $Y_{0.02}Ba_{0.38}Cu_{0.6}$ | $Y, Ba, Cu$     |
| C2 - 1.1    | $Y_2O_3$                    | $Y$ , trace 99% |
| C3 - 2.0    | "BaO"                       | Ba,             |
| C4 - 1.0    | $TiO_2$                     | $Ti$ , trace    |
| C5 - 2.0    | SrTiO <sub>3</sub> pre      | Sr, Ti, trace   |
| C6 - 1.0    | ↓<br>post-mix               | ↓               |
| C7 2.0      | DRC 123.                    | $Y, Ba, Cu$     |
| C8          | DD 123                      | $Y, Ba, Cu$     |
| C9          | off comp 2.11               |                 |

IBM Technical Notebook

5

'New' <sup>20.25</sup> 30 g GRINDING CHARGE OF  $\text{SrTiO}_3$  in mill (3:10)  
 off (4:17)  
 $\text{O}_2$ , compressed AIR,  $\text{CO}_2$  cylinders obtained w/ regulations  
 Ar

YIELD  $\rightarrow$  20.4 g  $\therefore$  must be some from old batch or  $\text{ZrO}_2$   
 COMBINED w/ OLD POWDER  $\rightarrow$  23 g of milled powder

12/2 C1. batch 45.6 grams left  
 39.56 g (16 g kept for files)  
 $\frac{10.5}{29.5}$  left for pellets  
 $\sim 10$  for grinding charge TFE/Toluene

NEW BOTTLES ORDERED, NO TEFLON AVAILABLE, - approx - 60 hrs total

$\text{SrTiO}_3$  pellets  $\rightarrow$  10-10 (24 hrs) down 4  $\therefore$  2-2 am (12:?) / 12-12 (24)

ST5, ST6 - start 10 AM, 12/10, numerous interruptions due to furnace malfunctions, out 12:00 PM, 12/10

ST5 edge chips 1 side OK otherwise 21 ISO.

\* 4.08 0.285 0.584  
 0.52

(401) 0.237 0.520 4.94 1.027  
 0.602 1.321 0.825

ST6 large chip during iso pressing in  $\frac{3}{4}$  side, must do

4.128 0.586 0.886  
~~0.510~~ ~~0.857~~

4.15 0.513 0.249 4.92 1.023  
 1.303 0.632(5) 0.843

\* blurring clock



6

IBM Technical Notebook

950C Run

|            |         |       |       |       |      |       |
|------------|---------|-------|-------|-------|------|-------|
| POST GREEN | C1P9    |       |       |       |      |       |
|            | 3.108   | 0.577 | 0.185 | 3.92  | 61.5 |       |
|            |         | 1.466 | 0.470 | 0.793 |      |       |
| POST       | 3.1     | 0.514 | 0.161 |       |      |       |
|            | no loss | 1.306 | 0.409 | 0.548 | 5.66 | 88.9% |
| GREEN      | DRC 2   | 0.579 | 0.177 |       |      |       |
|            | 3.204   | 1.471 | 0.450 | 0.765 | 4.19 | 65.8  |
| POST       | 3.2     | 0.551 | 0.165 |       |      |       |
|            | no loss | 1.400 | 0.419 | 0.645 | 4.96 | 77.9  |

12/7

pallets not in best shape after iso at 26000

975C Run

|         |                                   |       |       |       |       |             |
|---------|-----------------------------------|-------|-------|-------|-------|-------------|
| POST    | C1P10                             | 0.574 | 0.185 | 3.99  | 61.9  |             |
|         | 3.090                             | 1.458 | 0.470 | 0.785 |       |             |
|         | 3.056                             |       |       |       |       |             |
| POST    | 1% loss                           | 0.507 | 0.157 | 5.88  | 92.3  | PROBABLY 93 |
|         |                                   | 1.288 | 0.399 | 0.570 |       | +3.4%       |
| * DRC 3 |                                   | 0.579 | 0.181 | 4.24  | 66.6% | ~           |
|         | 3.318                             | 1.471 | 0.460 | 0.782 |       |             |
| POST    | crack still apparent, but holding |       |       |       |       |             |
|         | 3.293                             | 0.547 | 0.168 | 0.647 | 5.08  | 79.9 + 2%   |
|         | 0.75% loss                        | 1.389 | 0.427 |       |       |             |

C1P10 Pyrometer 91.8 → 92 : mostly closed porosity (95 if on pure density basis)

\* cracked in 1/2, but holding. Will go up if see if it heats.

To Temp @ 4:05 → 2 HRS 6:05 then ramp down

9:00 A.M 12/8 start cooling, OK NOT FLOWING WHEN ARRIVED, THOUGH COULD HAVE HAD BACK PRESSURE

IBM Technical Notebook

7/3 7

12-8

100% E/G mix  $\Rightarrow$  new wght calc.

(4.0 g) E basis (transferred to jar for physical mixing)

$$92.0913 \text{ g / mM section} \therefore \frac{4.0}{92.0913} = 0.0434 \text{ mM}$$

0.0434 mM is BASIS for mix of 0.7 mM E ectectic

$$0.0434 / 0.7 = 0.0620 \text{ mM total} \therefore 0.3 \text{ mM B11} \rightarrow$$

$$0.3 (0.0620) = 0.0186 \text{ mM} (94.6725 \text{ g / mM 211}) = 1.761 \text{ g 211}$$

$$\begin{array}{r} 1.761 \text{ g 211} \\ 4.0 \text{ g E} \\ \hline 5.761 \text{ g mix} \end{array}$$

$$\text{tare } 0.83 \quad \begin{array}{r} 5.76 \\ 5.68 \text{ recovered} \\ \hline 0.08 \text{ g loss on mixing} \end{array}$$

5.53 after gunding (slight loss) of transfer

1 pellet poured  $\Rightarrow$  EG1  $\Rightarrow$  to temp 12/10 @ 3:40-45 PROS OUT TO BE 5:45

$$\begin{array}{ccccccc} 2.57 & 0.580 & 0.153 & & 3.88 & \text{"0.9" } \Rightarrow 74\%? \\ & 1.473 & 0.389 & 0.663 & & \end{array}$$

Rel. density calc  $0.3 (6.00) + 0.7 (4.9) \Rightarrow 5.23$  approx theoretical  
 $\uparrow$  EMPIRICAL  $\uparrow$  D's

$$\begin{array}{ccccccc} 2.543 & \sim 0.611 & 0.161 & & 2.825 \\ (1\% \text{ wght loss}) & 1.55 & 0.480 & 0.90 & \end{array}$$

Restarted for overwrite RUN

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# IBM Technical Notebook

## III. DENSITY WORKSHEET

### STEREOPHONOMETRY TRUE POWDER DENSITY

SAMPLE I.D. R-3.687 DATE 12-9-87  
 SOURCE PRD OPERATOR PRD  
 TOTAL WEIGHT 18.855 g. OUTGASSING CONDITIONS  
 TARE WEIGHT 4.061 g.  
 SAMPLE WEIGHT 14.794 g. ADDED VOLUME,  $V_A$  cc  
 CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

| DATA              |           |       |
|-------------------|-----------|-------|
| RUN 1             | RUN 2     | RUN 3 |
| $P_2$ 18.362      | 18.488    |       |
| $P_3$ 4.980       | 5.013     |       |
| $V_p$ 7.023 cc    | 3.034 cc  |       |
| DENSITY 4.89 g/cc | 4.88 g/cc |       |

$\Delta 0.24$  (5%)  
 $2.65 \pm 5.13$   
 {same error}  
 {least squares}

16

## III. DENSITY WORKSHEET

### STEREOPHONOMETRY TRUE POWDER DENSITY

SAMPLE I.D. R-3.687 DATE 12-9-87  
 SOURCE PRD OPERATOR PRD  
 TOTAL WEIGHT 12.626 g. OUTGASSING CONDITIONS  
 TARE WEIGHT 4.061 g.  
 SAMPLE WEIGHT 8.565 g. ADDED VOLUME,  $V_A$  cc  
 CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

| DATA              |           |        |
|-------------------|-----------|--------|
| RUN 1             | RUN 2     | RUN 3  |
| $P_2$ 18.320      | 18.502    | 18.534 |
| $P_3$ 5.078       | 5.213     | 5.222  |
| $V_p$ - cc        | 1.296 cc  |        |
| DENSITY 4.15 g/cc | 3.96 g/cc |        |

POST-SUMMARY  
 $R-3.687$   
 $P_2$  18.501 18.44  
 $P_3$  5.087 5.079  
 $V_p$  2.419 2.394  
 $D$  4.05 (2.3%)  
 4.09  
 (3.3%)

16

## III. DENSITY WORKSHEET

### best guess - 5.9 STEREOPHONOMETRY TRUE POWDER DENSITY

SAMPLE I.D. 211 DATE 12-9-87  
 SOURCE PRD OPERATOR PRD  
 TOTAL WEIGHT 19.662 g. OUTGASSING CONDITIONS  
 TARE WEIGHT 4.061 g.  
 SAMPLE WEIGHT 15.601 g. ADDED VOLUME,  $V_A$  cc  
 CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

| DATA              |        |            |        |
|-------------------|--------|------------|--------|
| RUN 1             | RUN 2  | RUN 3      | RUN 4  |
| $P_2$ 18.557      | 18.568 | 18.584     | 18.529 |
| $P_3$ 5.084       | 5.085  | 5.052      | 5.058  |
| $V_p$ 2.578 cc    |        | 2.736 cc   | 2.798  |
| DENSITY 6.05 g/cc |        | 6.080 g/cc | 5.97   |

$\pm 0.3$   
 (5.95 - 6.35)\*  
 \*likely 6.05  
 (6.05 - 6.35) (least squares)

16

Ave.  $R_{\text{avg}}$  2  
 6.09

### STEREOPHONOMETRY TRUE POWDER DENSITY

SAMPLE I.D. 123 DATE 12-9-87  
 SOURCE PRD OPERATOR PRD  
 TOTAL WEIGHT 21.026 g. OUTGASSING CONDITIONS  
 TARE WEIGHT 4.061 g.  
 SAMPLE WEIGHT 16.965 g. ADDED VOLUME,  $V_A$  cc  
 CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

| DATA              |        |       |
|-------------------|--------|-------|
| RUN 1             | RUN 2  | RUN 3 |
| $P_2$ 18.598      | 18.596 |       |
| $P_3$ 5.078       | 5.078  |       |
| $V_p$ 2.73 cc     |        |       |
| DENSITY 6.21 g/cc |        |       |

16

The above understood  
 and witnessed by:

Date

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12/9

9

# IBM Technical Notebook

## III. DENSITY WORKSHEET

### STEREOPYCNOMETER TRUE POWDER DENSITY

SAMPLE I.D. 123-344 DATE 12-9  
SOURCE DIMANDS OPERATOR PRD  
TOTAL WEIGHT 19.700 g. OUTGASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 15.639 g. ADDED VOLUME,  $V_A$  85.52 cc  
CELL HOLDER VOLUME,  $V_C$  34.85 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

R-3.646 DATA  
RUN 1 RUN 2 RUN 3  
 $P_2$  18.603 18.561 18.561  
 $P_3$  5.103 5.091 5.091  
 $V_p$  2.923 cc cc cc  
DENSITY 6.199 g/cc g/cc g/cc

no purge

16

## III. DENSITY WORKSHEET

### STEREOPYCNOMETER RUN 2 TRUE POWDER DENSITY

SAMPLE I.D. 123 DATE 12-9  
SOURCE C1 OPERATOR PRD  
TOTAL WEIGHT 22.944 g. OUTGASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 18.883 g. ADDED VOLUME,  $V_A$  34.85 cc  
CELL HOLDER VOLUME,  $V_C$  85.52 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

R-3.671 DATA  
RUN 1 RUN 2 RUN 3  
 $P_2$  18.508 18.508 18.508  
 $P_3$  5.014 5.014 5.014  
 $V_p$  3.082 cc cc cc  
DENSITY 6.13 g/cc g/cc g/cc

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## III. DENSITY WORKSHEET

### STEREOPYCNOMETER TRUE POWDER DENSITY

SAMPLE I.D. 123 DATE 12-9-87  
SOURCE C1-344 OPERATOR PRD  
TOTAL WEIGHT 19.459 g. OUTGASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 10.396 g. ADDED VOLUME,  $V_A$  85.52 cc  
CELL HOLDER VOLUME,  $V_C$  34.85 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

R-3.58 DATA  
RUN 1 RUN 2 RUN 3  
 $P_2$  18.677 18.643 18.643  
 $P_3$  5.218 5.208 5.208  
 $V_p$  1.703 cc cc cc  
DENSITY 6.10 g/cc 6.105 g/cc g/cc

NOT BACK TO ZERO

16

### STEREOPYCNOMETER TRUE POWDER DENSITY

SAMPLE I.D. C1P10 DATE 12-10-87  
SOURCE C1-975242 OPERATOR PRD  
TOTAL WEIGHT 6.613 g. OUTGASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 2.552 g. ADDED VOLUME,  $V_A$  85.52 cc  
CELL HOLDER VOLUME,  $V_C$  34.85 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

R-3.485 DATA  
RUN 1 RUN 2 RUN 3  
 $P_2$  18.148 18.182 18.182  
 $P_3$  5.208 5.217 5.217  
 $V_p$  0.4355 cc cc cc  
DENSITY 5.899 g/cc g/cc g/cc

6.13 > 95.6  
6.37 > 91.8 (92)

16

7.668 + 38.75

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Date

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by

Date

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# IBM Technical Notebook

10  
12/10

Powders for Analysis  $\Rightarrow$  None entered @ conf. time  
 12/11, Sensitive NOT enough  
 Need to increase by 10X at least.

#1 - Species Description  
 $Y_2O_3$  left exposed to air

$TiO_2$

C1  $YBaCu$   
 $1 \ 2 \ 3$

DD1

DRC

P11

EI  $Y_{0.02}Ba_{0.23}Cu_{0.6}$

off comp

off comp

Table I - Precision<sup>1</sup> of Metals determined by ICP in  $La_{1-x}Sr_xCuO_4$  and  $YBa_2Cu_3O_7$  Thin Films.

| Element | $x^2$ | S.D. | R.S.D. (%) |
|---------|-------|------|------------|
| La      | 1.80  | 0.08 | 4.64       |
| Sr      | 0.20  | 0.01 | 5.52       |
| Cu      | 1.00  | 0.14 | 3.52       |
| Y       | 1.00  | 0.05 | 5.60       |
| Ba      | 2.04  | 0.07 | 3.43       |
| Cu      | 3.00  | 0.11 | 3.67       |

<sup>1</sup>Based on 7 determinations

<sup>2</sup>Calculated atomic ratios

For 123

Y (0.933)  $\Rightarrow \pm 0.019$  0.314 - 0.352

Ba (0.667)  $\Rightarrow \pm 0.023$  0.344 - 0.390

Cu (1.00)  $\Rightarrow \pm 0.036$  0.963 - 1.0367

The above understood  
and witnessed by

Date

and

Date

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possibly important disclosure of

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11

Theoretical wgt % calcs.

IBM Technical Notebook

$TiO_2 \Rightarrow 47.90/79.8988 \Rightarrow 59.95$

Anal 1

57.3

ERROR reported

$SrCO_3 \Rightarrow 87.62/147.62935 \Rightarrow 59.35$

ACT ANALYZED

$BaCO_3 \Rightarrow 137.34/197.34435 \Rightarrow 69.59(2)$

$BaO \Rightarrow$

89.566

88.9

99.26 !

$SrTiO_3 \Rightarrow Sr \Rightarrow 47.74(5)$   
 $Ti \Rightarrow 26.10(1)$

M.W. 183.5182

C5- 22.2  
 49.4

$Ti$   
 $Sr$

85.05% (15% poor)  
 "3.48% rich"

C6 24.2  
 50.6

$Ti$   
 $Sr$

92.72 (7.3% poor)  
 "5.98% rich"

86.5

92.5

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12/14 both well shaped pellets

C1P11 - 150 26

3.673      0.574      0.215      4.03      63.3  
                  1.458      0.546      0.9116

92+ <sup>final</sup> from T. SHAW

C1fp(#)? 15026

3.058      0.561      0.206      3.606      56.6 as usual  
                  1.437      0.523      0.848

- final microstructure full of liquid, but mod g.s. { cracking
- no final density recorded

12/15 pellets in furnace from 12/14 in expurge.  
 To temp (10°C/min ramp from RT) @ 10:50 A.M.  
 Low (leading) side undershoot 974, high (downside) overshoot 978.  
 Stable variation 974-976 ✓

start ramp down 1:00 p.m. (to 600C where soak for 48 hours)

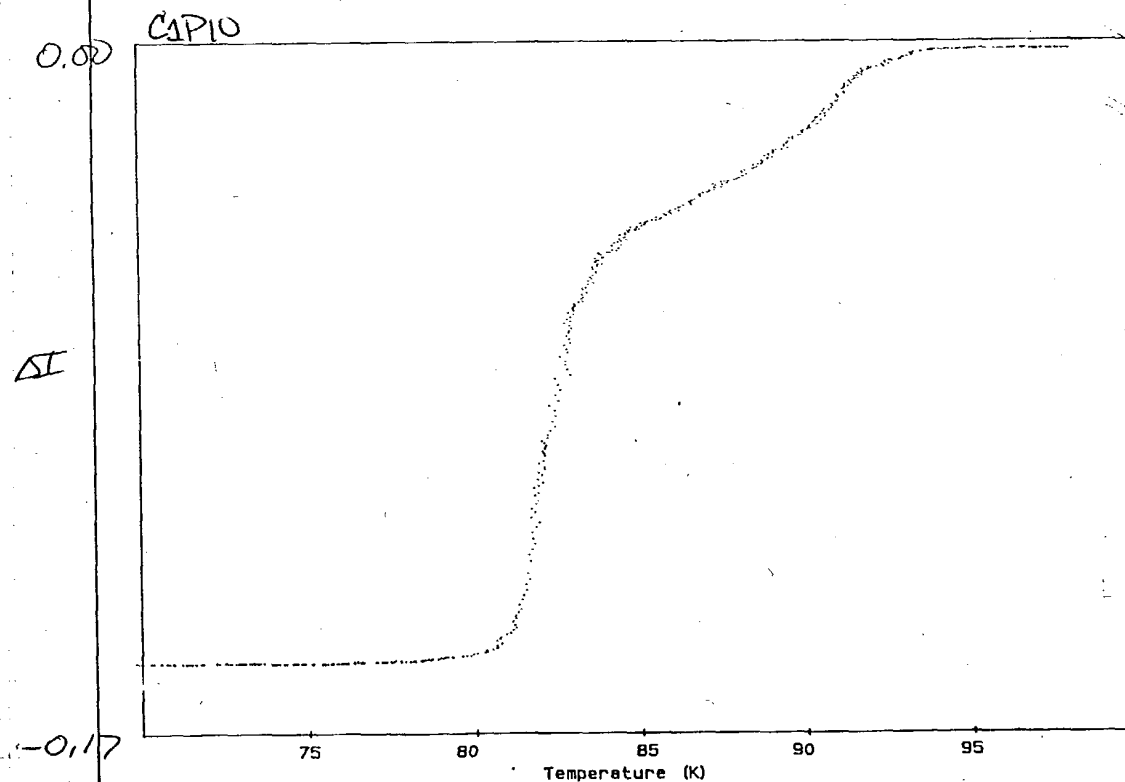
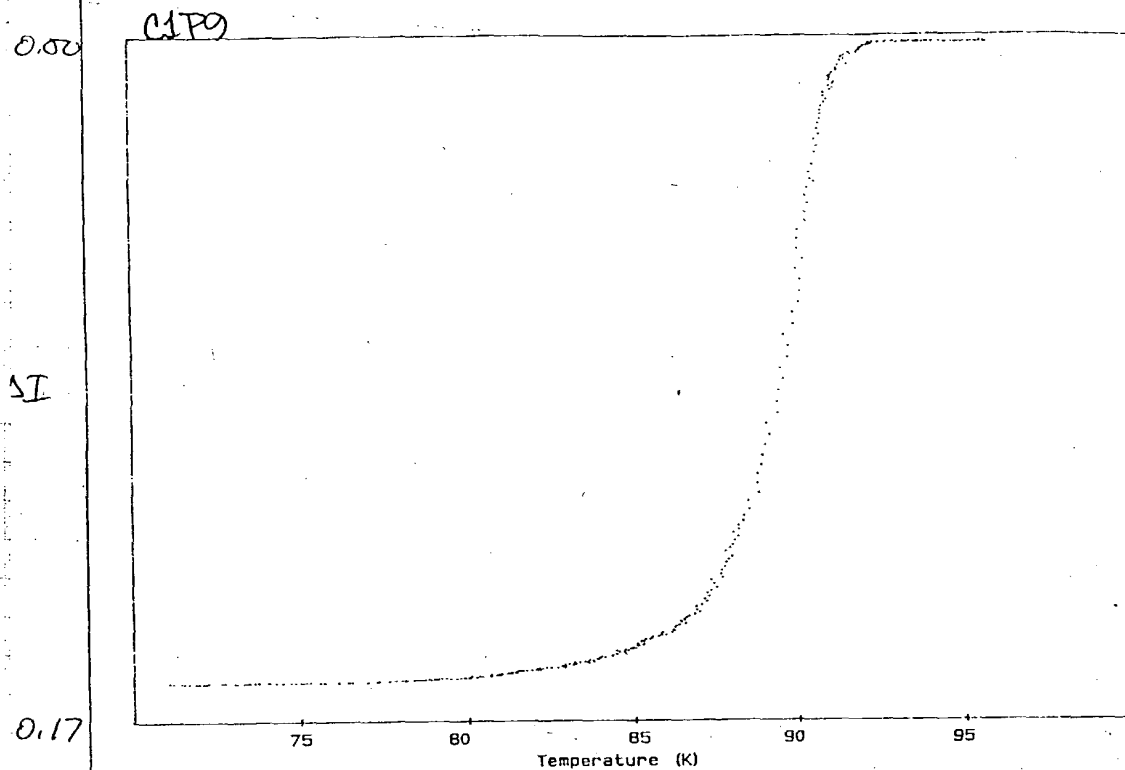
$$\left\{ \text{Diff coef: } 2 \times 10^{-15} \text{ m}^2/\text{s}^{-1} \times 2 \times 10^{-15} \frac{\text{m}^2}{\text{s}^2} \times \frac{t^2}{(0.3048 \text{ m})^2} = 2.153 \frac{t^2}{\text{s}^2} \times 10^{-14} \right\}$$

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14 C2 Batch  $\rightarrow \frac{1}{2} \text{Ba}_2\text{Cu}_3\text{O}_7$  200g

From C1 batch calc. (pg. 54 Book III)  $\rightarrow$  72 Book II

$\frac{1}{2} \text{O}_3 \Rightarrow$  wt. frac.  $17.1535 \Rightarrow$  Rec'dy  $17.1707 \Rightarrow$  Mult.  $\frac{1}{2}$  34.34

$\text{BaO}_x \Rightarrow$  46.5934 100  $\Rightarrow$  x2 93.1868

$\text{BaCO}_3$  conversion:  $93.1868 \frac{197.35}{153.31} = 119.932(3) \div 0.99 \Rightarrow$  121.14(4)

$\text{CuO} \Rightarrow$  36.25(8)  $\Rightarrow$  36.2893(1)  $\Rightarrow$  x2 72.57(9)

O.K. everything is Ba. ruled by analysis, so why not not correct  $\rightarrow$  119.93  
 Apply  $\frac{1}{2}$ .  $\text{BaCO}_3$  120.54

tare:  $\frac{219.67}{400.21} + \frac{120.54}{400.21}$  won't read, but will tare

reads: 120.57(4-6) over  $\frac{4}{5}$

$\text{CuO}$   
 tare: 0.87/7  
 reads: 72.58 transference quant. tare to zero w/ paper

$\frac{1}{2} \frac{1}{2}$  transference quant  
 34.34/5 paper weighs 0.1 when checked due to static glove charge, but after glove/charge removal 0.00. Think OK since cal. w/ inflated glove while (not more than 0.3% error)  
 Expected } 227.46 g dry  
 total right }

$\text{BaO}$  - 5.22 g/cc  $\text{BaCO}_3$  - 4.43  $\frac{1}{2} \text{O}_3$  - 5.01  $\text{CuO}$  - 6.3-6.49

$\therefore$  if bumping occurs w/ selective loss,  $\text{BaCO}_3$  should preferentially be lost if not ~~well~~ uniformly suspended.

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Except for 1 bump (0.06 g recovered)  $\Rightarrow$  very smooth, uneventful preparation. Placed in drying oven for weekend drying. (oven cleaned before use also)

12/21 After breaking up cake and re-baking under vac @ 70C for 3 hrs.

~~CRUX~~ #1 transference

ideally want 75 per cent

166.67  $\rightarrow$  0.97  
 tare  $\frac{86.21}{80.46}$   
 - .01 g "recovery"

totals  
 80.46  
 77.74  
 68.29

226.49 expected 227.46 (99.57%)

0.3 g recovered on ~~brushing~~ brushing blk.

CRUX 2  $\frac{172.72}{94.98}$   
 77.74  
 + .03 "recovery"

$\frac{226.79}{227.46}$  total 99.7%

CRUX 3  $\frac{173.46}{105.17}$  "white"  
 68.29

Rxn. Run 1  $\Rightarrow$  W { on @ 11:00pm 320 ramp to 940C, 450 cool ramp  
 14 hrs + 3 up + 2 down = 20 hrs total

12/22 11:00, 11:00, 11:00

{12/21}

IBM Technical Notebook

12/17-18 CENTURR ST<sub>2</sub>O<sub>3</sub> RUN

2100-1700 psi Ar usage 16 hr soak @ 1800 w/ 16.7 up/400 down ramp

Running Si-Christy RUN Prog. 05

So for 12/21 → (X) ST<sub>2</sub>O<sub>3</sub> RUN 24 hrs → 1000 psi

16  
 40 hrs → 1500 psi max permissible

Set for 36 → RAMP STARTED @ 11:25 p.m. 12/21

3  
 4:25  
 36 hours soak  
 10:25

1600 psi @ 300C RAMP up 4.25 hours total should be O.K.

(3 hrs → 1000) → 15,000 projected usage.

12/22 9:00 AM

19.3 soak hours left ∴ Δt → 16.7 + 3 → 19.7 (16-11250) psi → 4,750

∴ 241.1 psi/hr. 19.3 + 4.25 = 23.55 (241.1 psi/hr) = 5,680

11250 - 5680 = REMAINDER of 5,572 psi } could run longer if rate remains constant

6:00 PM

11,250 - 9,000 → 2,250 / (16.7 - 10.2) = 2250 / 6.5 = 346.2 !

346.2 (10.2 + 4.25) = 45,000 psi + (4000) = 4,000 to spare ✓

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12-22

C2 RXN seems good, NO APPARENT LIQUID, LARGE SHRINKAGE  
 NO VISIBLE GREEN, GOOD BLACK COLOR, BEFORE UNLOADING

~~Past weight.~~

CRUX #1  
 initial

166.97

tare

86.21

80.76

$$80.76 + (80.76 \times (-0.1182)) = 71.214$$

loss calc.

100%  
 EXPECTED RXN weight.

227.46 theoretical powder

$$\frac{120.54}{227.46} = 0.52994 \text{ weight \% } \text{BaCO}_3$$

CRUX #2  
 initial

172.72

94.98

77.74

as above

$$= 68.551$$

$$\frac{153.34}{197.35} (0.52994) = 0.41176$$

$$\Delta = 0.52994 - 0.41176 = 0.1182\% \text{ total}$$

↑  
WRONG?

CRUX #3

173.46

105.17

68.29

as above

$$= \frac{60.218}{199.983} \text{ total}$$

$$\frac{0.997}{0.997} = 200.58 \checkmark \text{ OK.}$$

Actual yields - 1A HR RXN @ 940C

CRUX #2  
 2.27g weight loss

170.45

94.98

85.47

total weight  
 initial tare

75.47

ABOVE EXPECTED  
 WEIGHT

6.919  
 (9.489)

% RXN

24.7

CRUX #1  
 2.05g weight loss

169.92

86.21

78.71

78.71

7.496  
 (9.546)

21.5

CRUX #3  
 1.55g weight loss

171.91

105.17

66.74

66.74

6.522  
 (8.072)

19.2

21.8% } O.K.  
 aver.

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18 *Recalc of wght loss calc.*

|  |   |
|--|---|
| $\begin{array}{r} \text{Bu } 137.34 \\ 0 \quad 15.9994 \\ \hline 153.3394 \approx 153.34 \\ \sim 153.34 \end{array}$ | $\begin{array}{r} \text{Bu } 137.34 \\ 30s \quad 47.9982 \\ \hline 12.01155 \\ \hline 197.34935 \\ \sim 197.35 \end{array}$ |
|--|---|

$$\frac{153.34}{197.35} = 0.776995 \quad (120.54) = 93.6589999 \quad 26.881 \text{ g}$$

$$26.881 \text{ g} / 3 \text{ cruc.} = \sim 8.96 \text{ g/crucible} \sim \text{correct}$$

Individual wght inquiries during grinding

12/29

aux 3 66.72 unloaded

$$\begin{array}{r} 105.17 \text{ tare} \\ 171.82 \text{ loaded} \\ \hline 171.91 \text{ previously} \\ \hline 0.09 \text{ g loss} \\ \hline 66.74 \end{array} \quad \text{loss} = 0.135\%$$

$$\begin{array}{r} 169.38 \\ 171.82 \\ \hline -2.44 \text{ loss} \\ \hline +1.55 \\ \hline 3.99 \end{array}$$

crux ②

$$\begin{array}{r} 86.20 \text{ tare (0.19/20)} \\ 78.75 \text{ load (-0.02) } 78.73 \\ \hline 78.69 \text{ gain after grinding} \\ \hline 0.06 \text{ g loss } > 0.076\% \text{ loss} \\ \hline 164.85 \\ \hline 78.65 \end{array} \quad 0.09 \text{ g loss} = 0.115\% \text{ loss}$$

$$\begin{array}{r} 161.68 \\ 164.85 \\ \hline -3.17 \text{ loss} \\ \hline +2.27 \\ \hline 5.44 \text{ total to date} \end{array}$$

crux ①

$$\begin{array}{r} 75.49/8 \text{ unloaded} \\ 94.99/8 \text{ tare} \\ \hline 75.46 \text{ load (precru)} \\ \hline 170.44 \text{ loaded.} \\ \hline 75.46 \end{array} \quad 0.03 \text{ loss}$$

$$\begin{array}{r} 167.18 \\ 170.44 \\ \hline -3.26 \text{ loss} \\ \hline 2.05 \\ \hline 5.31 \end{array}$$

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Samples were incompletely converted, as right loss indicated. Top was black but went through a transition of greens progressively over crucible. Grd powder was a dull forest green. Crux 1 slightly darker than 2 & 3. All had white hard oxides (presumably  $B_2O_3$ ). Tops inhibited oxygen flow throughout crucible. No tops used for second rxn. Heat treatment.

12/29 New losses consistent w/ crux loading. Conversion now up to 70.8 ~ 71%. Will reground and refine.

initial weighing loss

crux 2  
unloaded 95.02  
ground 72.10

crux 1 86.21 ✓  
grd. 75.40

crux 3 105.19  
grd post 64.15

crux 1 } 192.24 } 188.21 - 4.03 22.82 expected 26.807 (85.1%)  
(3 fuel load) } 86.20/1

crux 2 } 199.53 } 195.48 - 4.05  
95.01

12/24 Reground, to 1 crucible

$$\% (202.47 - 199.73) = 2.74 \text{ g loss (1.35\%)}$$

286.06  
86.27  
199.73 of 202.47 to start  
(before grd)

20 123 *Wght loss Summary* IBM Technical Notebook

| <i>Crucible #</i> | <i>Initial</i>          | <i>Post (1)</i> | <i>Post (2)</i> | <i>Post (3)</i> | <i>Crucible</i> |
|-------------------|-------------------------|-----------------|-----------------|-----------------|-----------------|
| 1                 | 80.76                   | 78.71           | 75.48           | 102.0           | 143             |
| 2                 | 77.74                   | 75.47           | 72.20           | 100.47          | 2               |
| 3                 | 68.29                   | 66.74           | 64.21           | 202.47          |                 |
| <i>thernet</i>    | <u>226.79</u><br>227.46 | 220.92          | 211.89          |                 |                 |

Final gnd into 1 crucible: pre 202.47  
 gnd post 199.73  
 loss 2.74g (1.35%  $\Rightarrow$  1g spill of saved powder)

Was 85% reacted before this run.  
 Total loss so far slightly less than 24.32g / 27.46 (88.5-85%)

Expect less than, but approx. 3.0 g loss for complete rxn.

0.52994%  $\text{BaCO}_3$  { (0.77695% of  $\text{BaCO}_3$  is  $\text{BaO}$ )

Look for 283 g total upon cooling!

1/5 initial wght.  $\frac{288.00}{284.17}$   $\frac{199.73}{197.59}$  initial unloaded  
 post  $\frac{284.17}{001.83g}$   $\frac{2.14}{}$

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1/4 SrTiO<sub>3</sub> synthesis <sup>IBM Technical Notebook</sup> references book III pgs. 77, A3

TiO<sub>2</sub> - 79.8988 g/M

SrCO<sub>3</sub> - 147.6235

SrTiO<sub>3</sub> - 183.5182

SrO - 103.6194

Ti - 47.90 IN SrTiO<sub>3</sub> 26.1009

Sr - 87.62 IN 47.7446

Take transferred amount to SHAKER JAR (SrCO<sub>3</sub>) as basis for TiO<sub>2</sub> addition.

$$\cancel{201.66 \text{ g base}} \frac{48.50}{147.6235} \times 0.32854 \text{ moles} \times 79.8988 \text{ g/M TiO}_2 = 26.2498 \text{ g} \\ = 26.25475$$

~~110.85~~

251.07  
 207.56  
 43.51

$$\frac{251.07}{26.25} \div 999 = \frac{251.07}{277.32} \text{ target } 277.3(5) \text{ actual } 277.35/6$$

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IBM Technical Notebook

COMPS SCRIPT A1 dated 87/12/02 14:32:25 ..... Page 1

Date: 2 December 1987, 13:24:31 EST  
From: PLECHAT at YKIVM2  
To: PRD

The laboratory results on your samples are:

|      |      |      |              |   |
|------|------|------|--------------|---|
| # C1 | Y    | Ba   | Cu O         | Cu=1, ICP   |
|      | 0.03 | 0.68 | X            |   |
| # C2 | Y    | ...  | 78.1 % (W/W) |   |
| # C3 | Ba   | ...  | 88.9 %       |   |
| # C4 | Ti   | ...  | 57.3 %       | / error due to static electr.<br>during weighing of sample/ |
| # C5 | Ti   | ...  | 22.2 %       |   |
|      | Sr   | ...  | 49.4 %       |   |
| # C6 | Ti   | ...  | 24.2 %       |   |
|      | Sr   | ...  | 50.6 %       |   |
| # C7 | Y    | Ba   | Cu O         | Cu=1  |
|      | 0.34 | 0.71 | X            |   |
| # C8 | Y    | Ba   | Cu O         |   |
|      | 0.34 | 0.71 | X            |   |
| # C9 | Y    | Ba   | Cu O         |   |
|      | 2.37 | 1.10 | X            |   |

MHP

Date: 21 October 1987, 10:45:18 EDT  
From: PLECHAT at YKIVM2  
To: PRD

The laboratory results on your samples are:

|       |      |      |      |           |
|-------|------|------|------|-----------|
| # C1  | Y    | Ba   | Cu O | Cu=1, ICP |
|       | 0.35 | 0.72 | X    |           |
| # C1f | Y    | Ba   | Cu O |           |
|       | 0.33 | 0.70 | X    |           |
| # C5  | Y    | Ba   | Cu O |           |
|       | 2.21 | 1.06 | X    |           |

Other results to follow from Olson,  
MHP

Note: I have produced a light green compound from 123 with  
the formula: Y Ba Cu O. If interested get in touch  
12 3 X  
with me.

*Handwritten:*  
T<sub>1</sub> consistently low 26.1  
Sr consistently high 47.7

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# IBM Technical Notebook

23

4 1/2  
283.17  
tare 86.61  
196.56

initial 197.59  
196.56  
1.03 g lost during grinding

Post  
196.56  
194.16  
-2.40

Lost another 2.4 g. Must be totally converted @ this point.

UNiaxial - 7,000 / 0.371 = 18,870 PSI

0.126 0.611 2.53 4.19 65.8  
0.320 1.55 0.604

C2P1 green  
no final dms. data

C2P2 → Will leave notes on push later. Too busy. Still see  
10. on crucible however, disheartening.

→ 1 mill 4.2 um PSD 10-1 ~ flat dist.

green 27150 pressed

3.59 0.580 0.194 4.274 67.1% (high vs. C1)  
1.473 0.493 0.84

C2P3- mill 2 2.53 um ave., much better behaved pellet  
(Green)

3.55 0.576 0.210 3.96 62.2% (good agreement w/ C1)  
1.463 0.533 0.896

C2P2- removed @ 600 °C → 20° up to 800, 10° to 975, 20° down

3.59 0.554 0.186 4.89 76.8% ! terrible  
1.407 0.472 0.734 slightly higher due to  
pellet attrition

1/13

C2P3 3.57 0.517 0.185 5.57  
1.313 0.47 0.636

~ 88

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IBM Technical Notebook

24 1/13

C2P4 3,775 unc/26,000 ISC 988 2HRS/600 over

3.50/1 0.576 0.206 3.987 62.6% consistent

1/14

3.49 0.515 0.180 5.68 89.2

1.308 0.457 0.614

C2P5 3775/24 990

3.18 0.577 0.199 3.74 58.7%

1.466 0.505 0.85

3.15 0.496 0.168 5.92 92.9

1.26 0.427 0.532

pellet has stress cracking and photo microstructure with  
 large grain interior and peripheral eggshell of small grains.

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pg 257  
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# IBM Technical Notebook

MODEL CPM-500  
 PARTICLE ANALYZER

DATE 11/4  
 SAMPLE 385  
 SOLVENT 150

CONDITIONS 1.5 ARS

SOLV. VISC 2.10 CP  
 SOLV. DENS 0.794 G/CC  
 SHIP. DENS 0.274 G/CC  
 DPMG 10.0 GPM  
 DPMG 1.00 GPM  
 DPMG 1.00 GPM  
 SPEED 500.000

TIME 0.0 4.00 15 SEC

DATA

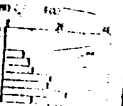
TIME RESPONSE



DISTRIBUTION TABLE (BY VOL.)

| DPMG       | FCL | FCL |
|------------|-----|-----|
| 0.0-0.5    | 0.0 | 0.0 |
| 0.5-1.0    | 0.0 | 0.0 |
| 1.0-1.5    | 0.0 | 0.0 |
| 1.5-2.0    | 0.0 | 0.0 |
| 2.0-2.5    | 0.0 | 0.0 |
| 2.5-3.0    | 0.0 | 0.0 |
| 3.0-3.5    | 0.0 | 0.0 |
| 3.5-4.0    | 0.0 | 0.0 |
| 4.0-4.5    | 0.0 | 0.0 |
| 4.5-5.0    | 0.0 | 0.0 |
| 5.0-5.5    | 0.0 | 0.0 |
| 5.5-6.0    | 0.0 | 0.0 |
| 6.0-6.5    | 0.0 | 0.0 |
| 6.5-7.0    | 0.0 | 0.0 |
| 7.0-7.5    | 0.0 | 0.0 |
| 7.5-8.0    | 0.0 | 0.0 |
| 8.0-8.5    | 0.0 | 0.0 |
| 8.5-9.0    | 0.0 | 0.0 |
| 9.0-9.5    | 0.0 | 0.0 |
| 9.5-10.0   | 0.0 | 0.0 |
| 10.0-10.5  | 0.0 | 0.0 |
| 10.5-11.0  | 0.0 | 0.0 |
| 11.0-11.5  | 0.0 | 0.0 |
| 11.5-12.0  | 0.0 | 0.0 |
| 12.0-12.5  | 0.0 | 0.0 |
| 12.5-13.0  | 0.0 | 0.0 |
| 13.0-13.5  | 0.0 | 0.0 |
| 13.5-14.0  | 0.0 | 0.0 |
| 14.0-14.5  | 0.0 | 0.0 |
| 14.5-15.0  | 0.0 | 0.0 |
| 15.0-15.5  | 0.0 | 0.0 |
| 15.5-16.0  | 0.0 | 0.0 |
| 16.0-16.5  | 0.0 | 0.0 |
| 16.5-17.0  | 0.0 | 0.0 |
| 17.0-17.5  | 0.0 | 0.0 |
| 17.5-18.0  | 0.0 | 0.0 |
| 18.0-18.5  | 0.0 | 0.0 |
| 18.5-19.0  | 0.0 | 0.0 |
| 19.0-19.5  | 0.0 | 0.0 |
| 19.5-20.0  | 0.0 | 0.0 |
| 20.0-20.5  | 0.0 | 0.0 |
| 20.5-21.0  | 0.0 | 0.0 |
| 21.0-21.5  | 0.0 | 0.0 |
| 21.5-22.0  | 0.0 | 0.0 |
| 22.0-22.5  | 0.0 | 0.0 |
| 22.5-23.0  | 0.0 | 0.0 |
| 23.0-23.5  | 0.0 | 0.0 |
| 23.5-24.0  | 0.0 | 0.0 |
| 24.0-24.5  | 0.0 | 0.0 |
| 24.5-25.0  | 0.0 | 0.0 |
| 25.0-25.5  | 0.0 | 0.0 |
| 25.5-26.0  | 0.0 | 0.0 |
| 26.0-26.5  | 0.0 | 0.0 |
| 26.5-27.0  | 0.0 | 0.0 |
| 27.0-27.5  | 0.0 | 0.0 |
| 27.5-28.0  | 0.0 | 0.0 |
| 28.0-28.5  | 0.0 | 0.0 |
| 28.5-29.0  | 0.0 | 0.0 |
| 29.0-29.5  | 0.0 | 0.0 |
| 29.5-30.0  | 0.0 | 0.0 |
| 30.0-30.5  | 0.0 | 0.0 |
| 30.5-31.0  | 0.0 | 0.0 |
| 31.0-31.5  | 0.0 | 0.0 |
| 31.5-32.0  | 0.0 | 0.0 |
| 32.0-32.5  | 0.0 | 0.0 |
| 32.5-33.0  | 0.0 | 0.0 |
| 33.0-33.5  | 0.0 | 0.0 |
| 33.5-34.0  | 0.0 | 0.0 |
| 34.0-34.5  | 0.0 | 0.0 |
| 34.5-35.0  | 0.0 | 0.0 |
| 35.0-35.5  | 0.0 | 0.0 |
| 35.5-36.0  | 0.0 | 0.0 |
| 36.0-36.5  | 0.0 | 0.0 |
| 36.5-37.0  | 0.0 | 0.0 |
| 37.0-37.5  | 0.0 | 0.0 |
| 37.5-38.0  | 0.0 | 0.0 |
| 38.0-38.5  | 0.0 | 0.0 |
| 38.5-39.0  | 0.0 | 0.0 |
| 39.0-39.5  | 0.0 | 0.0 |
| 39.5-40.0  | 0.0 | 0.0 |
| 40.0-40.5  | 0.0 | 0.0 |
| 40.5-41.0  | 0.0 | 0.0 |
| 41.0-41.5  | 0.0 | 0.0 |
| 41.5-42.0  | 0.0 | 0.0 |
| 42.0-42.5  | 0.0 | 0.0 |
| 42.5-43.0  | 0.0 | 0.0 |
| 43.0-43.5  | 0.0 | 0.0 |
| 43.5-44.0  | 0.0 | 0.0 |
| 44.0-44.5  | 0.0 | 0.0 |
| 44.5-45.0  | 0.0 | 0.0 |
| 45.0-45.5  | 0.0 | 0.0 |
| 45.5-46.0  | 0.0 | 0.0 |
| 46.0-46.5  | 0.0 | 0.0 |
| 46.5-47.0  | 0.0 | 0.0 |
| 47.0-47.5  | 0.0 | 0.0 |
| 47.5-48.0  | 0.0 | 0.0 |
| 48.0-48.5  | 0.0 | 0.0 |
| 48.5-49.0  | 0.0 | 0.0 |
| 49.0-49.5  | 0.0 | 0.0 |
| 49.5-50.0  | 0.0 | 0.0 |
| 50.0-50.5  | 0.0 | 0.0 |
| 50.5-51.0  | 0.0 | 0.0 |
| 51.0-51.5  | 0.0 | 0.0 |
| 51.5-52.0  | 0.0 | 0.0 |
| 52.0-52.5  | 0.0 | 0.0 |
| 52.5-53.0  | 0.0 | 0.0 |
| 53.0-53.5  | 0.0 | 0.0 |
| 53.5-54.0  | 0.0 | 0.0 |
| 54.0-54.5  | 0.0 | 0.0 |
| 54.5-55.0  | 0.0 | 0.0 |
| 55.0-55.5  | 0.0 | 0.0 |
| 55.5-56.0  | 0.0 | 0.0 |
| 56.0-56.5  | 0.0 | 0.0 |
| 56.5-57.0  | 0.0 | 0.0 |
| 57.0-57.5  | 0.0 | 0.0 |
| 57.5-58.0  | 0.0 | 0.0 |
| 58.0-58.5  | 0.0 | 0.0 |
| 58.5-59.0  | 0.0 | 0.0 |
| 59.0-59.5  | 0.0 | 0.0 |
| 59.5-60.0  | 0.0 | 0.0 |
| 60.0-60.5  | 0.0 | 0.0 |
| 60.5-61.0  | 0.0 | 0.0 |
| 61.0-61.5  | 0.0 | 0.0 |
| 61.5-62.0  | 0.0 | 0.0 |
| 62.0-62.5  | 0.0 | 0.0 |
| 62.5-63.0  | 0.0 | 0.0 |
| 63.0-63.5  | 0.0 | 0.0 |
| 63.5-64.0  | 0.0 | 0.0 |
| 64.0-64.5  | 0.0 | 0.0 |
| 64.5-65.0  | 0.0 | 0.0 |
| 65.0-65.5  | 0.0 | 0.0 |
| 65.5-66.0  | 0.0 | 0.0 |
| 66.0-66.5  | 0.0 | 0.0 |
| 66.5-67.0  | 0.0 | 0.0 |
| 67.0-67.5  | 0.0 | 0.0 |
| 67.5-68.0  | 0.0 | 0.0 |
| 68.0-68.5  | 0.0 | 0.0 |
| 68.5-69.0  | 0.0 | 0.0 |
| 69.0-69.5  | 0.0 | 0.0 |
| 69.5-70.0  | 0.0 | 0.0 |
| 70.0-70.5  | 0.0 | 0.0 |
| 70.5-71.0  | 0.0 | 0.0 |
| 71.0-71.5  | 0.0 | 0.0 |
| 71.5-72.0  | 0.0 | 0.0 |
| 72.0-72.5  | 0.0 | 0.0 |
| 72.5-73.0  | 0.0 | 0.0 |
| 73.0-73.5  | 0.0 | 0.0 |
| 73.5-74.0  | 0.0 | 0.0 |
| 74.0-74.5  | 0.0 | 0.0 |
| 74.5-75.0  | 0.0 | 0.0 |
| 75.0-75.5  | 0.0 | 0.0 |
| 75.5-76.0  | 0.0 | 0.0 |
| 76.0-76.5  | 0.0 | 0.0 |
| 76.5-77.0  | 0.0 | 0.0 |
| 77.0-77.5  | 0.0 | 0.0 |
| 77.5-78.0  | 0.0 | 0.0 |
| 78.0-78.5  | 0.0 | 0.0 |
| 78.5-79.0  | 0.0 | 0.0 |
| 79.0-79.5  | 0.0 | 0.0 |
| 79.5-80.0  | 0.0 | 0.0 |
| 80.0-80.5  | 0.0 | 0.0 |
| 80.5-81.0  | 0.0 | 0.0 |
| 81.0-81.5  | 0.0 | 0.0 |
| 81.5-82.0  | 0.0 | 0.0 |
| 82.0-82.5  | 0.0 | 0.0 |
| 82.5-83.0  | 0.0 | 0.0 |
| 83.0-83.5  | 0.0 | 0.0 |
| 83.5-84.0  | 0.0 | 0.0 |
| 84.0-84.5  | 0.0 | 0.0 |
| 84.5-85.0  | 0.0 | 0.0 |
| 85.0-85.5  | 0.0 | 0.0 |
| 85.5-86.0  | 0.0 | 0.0 |
| 86.0-86.5  | 0.0 | 0.0 |
| 86.5-87.0  | 0.0 | 0.0 |
| 87.0-87.5  | 0.0 | 0.0 |
| 87.5-88.0  | 0.0 | 0.0 |
| 88.0-88.5  | 0.0 | 0.0 |
| 88.5-89.0  | 0.0 | 0.0 |
| 89.0-89.5  | 0.0 | 0.0 |
| 89.5-90.0  | 0.0 | 0.0 |
| 90.0-90.5  | 0.0 | 0.0 |
| 90.5-91.0  | 0.0 | 0.0 |
| 91.0-91.5  | 0.0 | 0.0 |
| 91.5-92.0  | 0.0 | 0.0 |
| 92.0-92.5  | 0.0 | 0.0 |
| 92.5-93.0  | 0.0 | 0.0 |
| 93.0-93.5  | 0.0 | 0.0 |
| 93.5-94.0  | 0.0 | 0.0 |
| 94.0-94.5  | 0.0 | 0.0 |
| 94.5-95.0  | 0.0 | 0.0 |
| 95.0-95.5  | 0.0 | 0.0 |
| 95.5-96.0  | 0.0 | 0.0 |
| 96.0-96.5  | 0.0 | 0.0 |
| 96.5-97.0  | 0.0 | 0.0 |
| 97.0-97.5  | 0.0 | 0.0 |
| 97.5-98.0  | 0.0 | 0.0 |
| 98.0-98.5  | 0.0 | 0.0 |
| 98.5-99.0  | 0.0 | 0.0 |
| 99.0-99.5  | 0.0 | 0.0 |
| 99.5-100.0 | 0.0 | 0.0 |

DISTRIBUTION GRAPH (BY VOL.)



MODEL CPM-500  
 PARTICLE ANALYZER

DATE 11/4  
 SAMPLE 385  
 SOLVENT 150

CONDITIONS

SOLV. VISC 2.10 CP  
 SOLV. DENS 0.794 G/CC  
 SHIP. DENS 0.274 G/CC  
 DPMG 10.0 GPM  
 DPMG 1.00 GPM  
 DPMG 1.00 GPM  
 SPEED 500.000

TIME 0.0 4.00 15 SEC

DATA

TIME RESPONSE



DISTRIBUTION TABLE (BY VOL.)

| DPMG      | FCL | FCL |
|-----------|-----|-----|
| 0.0-0.5   | 0.0 | 0.0 |
| 0.5-1.0   | 0.0 | 0.0 |
| 1.0-1.5   | 0.0 | 0.0 |
| 1.5-2.0   | 0.0 | 0.0 |
| 2.0-2.5   | 0.0 | 0.0 |
| 2.5-3.0   | 0.0 | 0.0 |
| 3.0-3.5   | 0.0 | 0.0 |
| 3.5-4.0   | 0.0 | 0.0 |
| 4.0-4.5   | 0.0 | 0.0 |
| 4.5-5.0   | 0.0 | 0.0 |
| 5.0-5.5   | 0.0 | 0.0 |
| 5.5-6.0   | 0.0 | 0.0 |
| 6.0-6.5   | 0.0 | 0.0 |
| 6.5-7.0   | 0.0 | 0.0 |
| 7.0-7.5   | 0.0 | 0.0 |
| 7.5-8.0   | 0.0 | 0.0 |
| 8.0-8.5   | 0.0 | 0.0 |
| 8.5-9.0   | 0.0 | 0.0 |
| 9.0-9.5   | 0.0 | 0.0 |
| 9.5-10.0  | 0.0 | 0.0 |
| 10.0-10.5 | 0.0 | 0.0 |
| 10.5-11.0 | 0.0 | 0.0 |
| 11.0-11.5 | 0.0 | 0.0 |
| 11.5-12.0 | 0.0 | 0.0 |
| 12.0-12.5 | 0.0 | 0.0 |
| 12.5-13.0 | 0.0 | 0.0 |
| 13.0-13.5 | 0.0 | 0.0 |
| 13.5-14.0 | 0.0 | 0.0 |
| 14.0-14.5 | 0.0 | 0.0 |
| 14.5-15.0 | 0.0 | 0.0 |
| 15.0-15.5 | 0.0 | 0.0 |
| 15.5-16.0 | 0.0 | 0.0 |
| 16.0-16.5 | 0.0 | 0.0 |
| 16.5-17.0 | 0.0 | 0.0 |
| 17.0-17.5 | 0.0 | 0.0 |
| 17.5-18.0 | 0.0 | 0.0 |
| 18.0-18.5 | 0.0 | 0.0 |
| 18.5-19.0 | 0.0 | 0.0 |
| 19.0-19.5 | 0.0 | 0.0 |
| 19.5-20.0 | 0.0 | 0.0 |
| 20.0-20.5 | 0.0 | 0.0 |
| 20.5-21.0 | 0.0 | 0.0 |
| 21.0-21.5 | 0.0 | 0.0 |
| 21.5-22.0 | 0.0 | 0.0 |
| 22.0-22.5 | 0.0 | 0.0 |
| 22.5-23.0 | 0.0 | 0.0 |
| 23.0-23.5 | 0.0 | 0.0 |
| 23.5-24.0 | 0.0 | 0.0 |
| 24.0-24.5 | 0.0 | 0.0 |
| 24.5-25.0 | 0.0 | 0.0 |
| 25.0-25.5 | 0.0 | 0.0 |
| 25.5-26.0 | 0.0 | 0.0 |
| 26.0-26.5 | 0.0 | 0.0 |
| 26.5-27.0 | 0.0 | 0.0 |
| 27.0-27.5 | 0.0 | 0.0 |
| 27.5-28.0 | 0.0 | 0.0 |
| 28.0-28.5 | 0.0 | 0.0 |
| 28.5-29.0 | 0.0 | 0.0 |
| 29.0-29.5 | 0.0 | 0.0 |
| 29.5-30.0 | 0.0 | 0.0 |
| 30.0-30.5 | 0.0 | 0.0 |
| 30.5-31.0 | 0.0 | 0.0 |
| 31.0-31.5 | 0.0 | 0.0 |
| 31.5-32.0 | 0.0 | 0.0 |
| 32.0-32.5 | 0.0 | 0.0 |
| 32.5-33.0 | 0.0 | 0.0 |
| 33.0-33.5 | 0.0 | 0.0 |
| 33.5-34.0 | 0.0 | 0.0 |
| 34.0-34.5 | 0.0 | 0.0 |
| 34.5-35.0 | 0.0 | 0.0 |
| 35.0-35.5 | 0.0 | 0.0 |
| 35.5-36.0 | 0.0 | 0.0 |
| 36.0-36.5 | 0.0 | 0.0 |
| 36.5-37.0 | 0.0 | 0.0 |
| 37.0-37.5 | 0.0 | 0.0 |
| 37.5-38.0 | 0.0 | 0.0 |
| 38.0-38.5 | 0.0 | 0.0 |
| 38.5-39.0 | 0.0 | 0.0 |
| 39.0-39.5 | 0.0 | 0.0 |
| 39.5-40.0 | 0.0 | 0.0 |
| 40.0-40.5 | 0.0 | 0.0 |
| 40.5-41.0 | 0.0 | 0.0 |
| 41.0-41.5 | 0.0 | 0.0 |
| 41.5-42.0 | 0.0 | 0.0 |
| 42.0-42.5 | 0.0 | 0.0 |
| 42.5-43.0 | 0.0 | 0.0 |
| 43.0-43.5 | 0.0 | 0.0 |
| 43.5-44.0 | 0.0 | 0.0 |
| 44.0-44.5 | 0.0 | 0.0 |
| 44.5-45.0 | 0.0 | 0.0 |
| 45.0-45.5 | 0.0 | 0.0 |
| 45.5-46.0 | 0.0 | 0.0 |
| 46.0-46.5 | 0.0 | 0.0 |
| 46.5-47.0 | 0.0 | 0.0 |
| 47.0-47.5 | 0.0 | 0.0 |
| 47.5-48.0 | 0.0 | 0.0 |
| 48.0-48.5 | 0.0 | 0.0 |
| 48.5-49.0 | 0.0 | 0.0 |
| 49.0-49.5 | 0.0 | 0.0 |
| 49.5-50.0 | 0.0 | 0.0 |
| 50.0-50.5 | 0.0 | 0.0 |
| 50.5-51.0 | 0.0 | 0.0 |

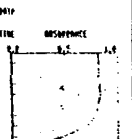
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## 27

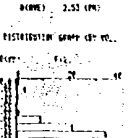
UNITED STATES  
PARTICLE ANALYZER  
DATE 1/17/88  
SAMPLE C2: PRO II

POSITIONS

|           |            |
|-----------|------------|
| SALV. 01% | 2.10:59    |
| SALV. 2   | 6.79:6:00  |
| SALV. 3   | 6.27:06:00 |
| B+        | 10.0:59    |
| B         | 2.00:59    |
| B-        | 2.00:59    |



| 0 (PM)     | 1 (L) | 2 (L) |
|------------|-------|-------|
| 10.0 - 9.0 | 0.0   | 0.0   |
| 9.0 - 8.0  | 0.7   | 0.7   |
| 8.0 - 7.0  | 2.5   | 2.5   |
| 7.0 - 6.0  | 4.0   | 4.0   |
| 6.0 - 5.0  | 0.0   | 3.6   |
| 5.0 - 4.0  | 0.0   | 3.6   |
| 4.0 - 3.0  | 0.7   | 4.3   |
| 3.0 - 2.0  | 26.8  | 34.3  |
| 2.0 - 1.0  | 35.5  | 67.6  |
| 1.0 - 0.0  | 24.6  | 32.4  |
| 0.0 - 0.0  | 7.6   | 100.0 |



Date \_\_\_\_\_

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 anything every entry. Have every possibly important  
 ed. Submit an Invention Disclosure of  
 possibly new and inventive.

28/1/9 (18,17,16,15 26.5g)

IBM Technical Notebook

NOTE → C1 powder

C1P12, 13, 14, 15

3.775/26.5

C1P12

|      |       |       |          |        |
|------|-------|-------|----------|--------|
| 3.04 | 0.574 | 0.178 | 3.92     | 61.5%  |
|      | 1.478 | 0.452 | 0.7755   |        |
| 3.01 | 0.506 | 0.153 | 5.966    | 93.66% |
|      | 1.285 | 0.389 | 0.504(5) |        |

C1P13

|      |       |          |         |       |
|------|-------|----------|---------|-------|
| 3.00 | 0.574 | 0.175    | 3.93(4) | 61.8% |
|      | 1.478 | 0.444(5) | 0.7626  |       |
| 2.97 | 0.506 | 0.150    | 6.01    | 94.35 |
|      | 1.285 | 0.381    | 0.494   |       |

C1P14(\*)

|      |       |       |         |       |
|------|-------|-------|---------|-------|
| 2.89 | 0.574 | 0.169 | 3.92(7) | 61.6% |
|      | 1.478 | 0.429 | 0.736   |       |

C1P15(\*)

|      |          |       |          |       |
|------|----------|-------|----------|-------|
| 3.05 | 0.575    | 0.179 | 4.00     | 62.8% |
|      | 1.460(7) | 0.455 | 0.762(7) |       |

(\*) NO DATA ON final pellets - Tom took

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 and witnessed by

Date

and  
 by

Date

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possibly important disclosure of

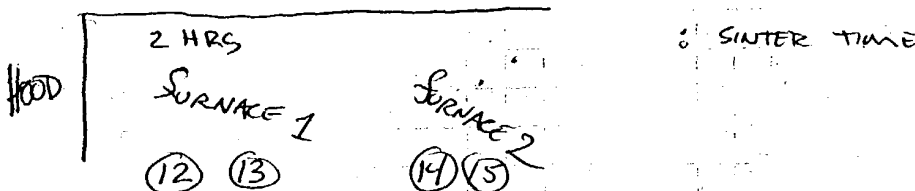
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# IBM Technical Notebook

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1/19 RUNS IN FURNACE as: all ramps 10°C/min



1/19 A.M.

↓  
 4:10 P.M. 4:25 P.M.  
 to temp (975°C)  
 6:15 P.M.  
 Ramp down to 600°C soak  
 1/20 1:49 P.M.  
 Ramp down to RT  
 check 2:22 (270°C)

Pellet thickness experiment DD mill powder 3275/26,000

DT 2.0

|      |          |       |       |        |
|------|----------|-------|-------|--------|
| 2.04 | 0.575    | 0.119 | 4.03  | 63.3 % |
| 2.01 | 1.460(5) | 0.302 | 0.506 |        |
|      | 0.507    | 0.100 | 6.09  |        |
|      | 1.288    | 0.234 | 0.33  | 95.6   |

DT 1.5

|      |          |          |       |         |
|------|----------|----------|-------|---------|
| 1.54 | 0.575    | 0.090    | 4.01  | 62.95 % |
| 1.51 | 1.460(5) | 0.229    | 0.384 |         |
|      | 0.509    | 0.075    | 6.04  | 94.8    |
|      | 1.293    | 0.190(5) | 0.250 |         |

DT 1.0 K

|      |          |       |       |        |
|------|----------|-------|-------|--------|
| 1.09 | 0.575    | 0.065 | 3.95  | 62.0 % |
|      | 1.460(5) | 0.165 | 0.276 |        |

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and by

Date



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 anything possibly new and inventive.

30

IBM Technical Notebook

Cutting CALCULATIONS for C1P12, B

$$\begin{array}{r} 0.503 \\ 0.06 \\ \hline 0.443/3 = 0.148 \end{array} \quad 3 \text{ blade thickness} + 0.05$$

C1P12  $(0.025) 5 = 0.125$   
 $(\downarrow) 6 = 0.150 \leftarrow \text{O.K. from micrometer}$

use 2 cuts { no 'parallelism' }

$$\begin{array}{r} 0.050 \\ 0.040 \\ \hline 0.11/3 = 0.037 + 0.015 = 0.0517 \end{array} \quad \text{10 from edge}$$

1 cut MADE, BUT PELLET HAS CRACK

$$\begin{array}{r} (0.025) 6 = 0.150 \\ 0.040 \\ \hline 0.19/3 = 0.037 + 0.015 = 0.052 \end{array}$$

1/21

DT 1.751 in furnace/no green data (5°C RAMP to try to eliminate sinter-cracking)

DT 1.25(2)

1.88

2.575

0.111

3.98

62.5

never run

1.4605

0.282

0.472

The above understood  
 and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
 by \_\_\_\_\_

Date \_\_\_\_\_

Date and sign every entry. Have entry witnessed. Submit an invention anything possibly new and inventive.

possibly important closure of

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# IBM Technical Notebook

31

Stereopycnometer

1/27/88 {25/26 supply, miller repair}  
 28  
 29, 2/01

See sheets

Data Points (Multiples)

| "    | D <sub>m</sub> |                   | D <sub>p</sub> |
|------|----------------|-------------------|----------------|
| "83" | 82.95          | DRC, DDP12        | 95.8           |
| "86" | 86.4           | JP262, C1P3, C1P2 | 92.2           |
| "89" | 89.3           | C1P1, C1P4, C1P7  | 89.56          |
| "91" | 91.3           | C1P1, C1P5, C1P8  | 91.9           |

NOTE pad: 97.3 - 95.8

←  $\Delta 86.4 - 89.3 = \Delta 3\%$

Single Point trends ⊗

|      |      |       |             |   |
|------|------|-------|-------------|---|
| 87.5 | 87.5 | JP1   | 83          | NOT clear, <sup>seems to</sup> <del>could</del> be closed |
| 77   |      | C2P2  | 95.4        | definitely wide open                                      |
| "93" | 93   | DDP13 | <u>86.6</u> | indicates closure   |

⊗ small volumes yield low D values for closed porosity.

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and by

Date

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32

3500/26,000

IBM Technical Notebook

2/02 Sintering: Porosity Inquiry C1 & C2 @ 975

{ 10°/min Ramp from RT, 2 HOUR SOAK, 10°/min to RT no O<sub>2</sub> equilibration. In order from left to right in row,

C1P16

|      |          |       |       |      |             |                   |
|------|----------|-------|-------|------|-------------|-------------------|
| 3.03 | 0.575    | 0.178 |       | 4.00 | 62.8        | } <u>polished</u> |
|      | 1.460(5) | 0.452 | 0.757 |      |             |                   |
| 3.00 | 0.500    | 0.152 |       | 5.92 | <u>92.9</u> |                   |
|      | 1.293    | 0.386 | 0.507 |      |             |                   |

C1P17

|      |          |        |          |      |             |                   |
|------|----------|--------|----------|------|-------------|-------------------|
| 3.26 | 0.575    | 0.191  |          | 4.01 | 62.9(5)     | } <u>polished</u> |
|      | 1.460(5) | 0.485  | 0.812(5) |      |             |                   |
| 3.22 | 0.508    | 0.164  |          | 5.94 | <u>92.8</u> |                   |
|      | 1.290    | 0.4166 | 0.544(5) |      |             |                   |

C2P6

|      |          |       |          |         |             |                   |
|------|----------|-------|----------|---------|-------------|-------------------|
|      | 0.575    | 0.191 |          | 3.82(6) | 60.0        | } <u>polished</u> |
| 3.16 | 1.460(5) | 0.493 | 0.826    |         |             |                   |
| 3.11 | 0.497    | 0.160 |          | 6.42    | <u>96.1</u> |                   |
|      | 1.262    | 0.406 | 0.507(8) |         |             |                   |

C2P7 <sup>chip</sup>

|      |          |          |       |       |             |                   |
|------|----------|----------|-------|-------|-------------|-------------------|
|      | 0.575    | 0.199    |       | 3.79  | 59.5        | } <u>polished</u> |
| 3.21 | 1.460(5) | 0.505(5) | 0.847 |       |             |                   |
| 3.16 | 0.497    | 0.164    |       | 6.065 | <u>95.2</u> |                   |
|      | 1.262    | 0.4166   | 0.521 |       |             |                   |

C2P7 good & dense, but exterior cracking due to oxygen penetration. Will guide cool by opening furnace. Quench.

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ITEM

C2-8 3.08 0.573 0.191 3.82  
1.455 0.485 0.806  
3.06(5) 0.529 0.158 5.53  
1.328 0.399 0.553

59.97  $\Rightarrow$  ~60%  
comparable to previous  
see  
86.8

C1-18 3.07 0.578 0.178 4.01  
1.468 0.452 0.765  
3.03 0.497 0.158 6.04  
1.262 0.401 0.5016

62.95 ~ 63%  
comparable to previous  
94.8

2/12

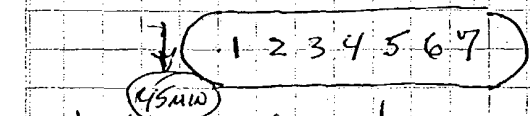
HP-4 green 5,000/27,000

13.98 0.947 ~0.301 4.02(5) 63.2  
2.405 0.764(5) 3.473

Cling C2-8 dry  
1<sup>st</sup> 0.50

Boat Spots  $\rightarrow$  positioning I.D.

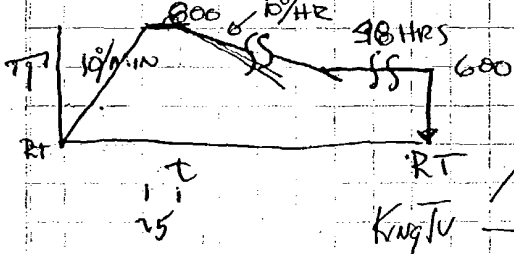
2/15



1. } large grain  
2. } material

{ C2 3/4

Heat Treatment



3. } C2 std. w/ surface cracking (outer)  
4. } inner surfaces should be d.k.

5. Good C2 top slice - no surface cracking

6. middle slice of 3/4 (w/ chip)

7. bottom slice of C2-5 above.

START: 4:50 PM 2/12  $\rightarrow$  6:15 2/12 start ramp down 20 HRS to soak point  
7:00  
2:50 2/15 ~ 30 HRS

QUENCH: 2:50 2/15

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34 2/17 3500/26750

|      |      |          |       |       |      |        |
|------|------|----------|-------|-------|------|--------|
| C2-9 | 3.09 | 0.575    | 0.193 |       | 3.76 | 59.0%  |
|      |      | 1.460(5) | 0.190 | 0.821 |      |        |
|      | 3.06 | 0.510    | 0.168 |       |      | 85.5 ! |
|      |      | 1.295    | 0.427 | 0.562 |      |        |

|       |       |          |       |          |      |                 |
|-------|-------|----------|-------|----------|------|-----------------|
| C2-10 | 3.06  | 0.575    | 0.191 |          | 3.77 | 59.2%           |
|       |       | 1.460(5) | 0.485 | 0.812(5) |      |                 |
|       | 3.025 | 0.501    | 0.164 |          | 5.72 | <del>90.6</del> |
|       | 3     | 1.272(5) | 0.417 | 0.530    |      | 89.6            |

Furnace Oz purge > 1 HR @ 29 C<sup>(32)</sup> 12:10 P.M., ∴ 945/10 =  
 94.5 mins / 60 min / HR = 1.575 HRS OR 1 hr 34.5 mins (1:45 START  
 1:45 - 2:15 (1/2 hr sinter) w/ quench. SINTER)

|       |      |          |          |       |       |            |
|-------|------|----------|----------|-------|-------|------------|
| C2-11 | 3.02 | 0.575    | 0.188    |       | 3.775 | 59.3% O.K. |
|       |      | 1.460(5) | 0.477(5) | 0.80  |       |            |
|       | 2.98 | 0.505    | 0.159    |       | 5.71  | 89.64 ~90  |
|       |      | 1.283    | 0.404    | 0.522 |       |            |

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$D \leq 4 \mu m$

$D \leq 6 \mu m$

$D \leq 6-7$

$D \leq 9$

35

IBM Technical Notebook

MODEL CRPA-SEP  
PARTICLE ANALYZER

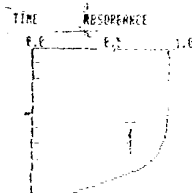
DATE 2/18  
SAMPLE C2-III OF  
SOLVENT ISO  
 $D = 0.83$

• CONDITIONS

SOLV. RATE 1.38 (LPM)  
SOLV. DENS 0.796 (G/CC)  
SAMP. DENS 0.376 (G/CC)  
DENSITY 10.0 (G/CC)  
PARKING 1.00 (LPM)  
DARKING 1.00 (LPM)  
SPEED 500 (RPM)

• TIME 6.4 MIN. 15 SEC

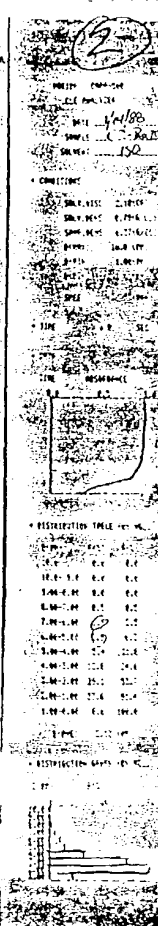
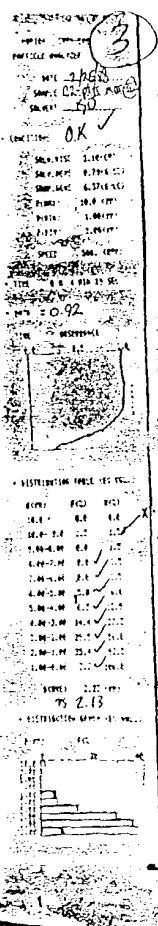
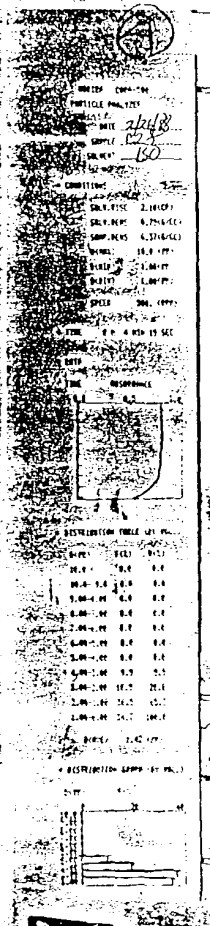
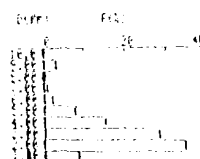
• DATE



• DISTRIBUTION TABLE (BY VOL.)

| DEPT     | FEED | FEED |
|----------|------|------|
| 10.0-9.0 | 0.0  | 0.0  |
| 9.0-8.0  | 0.0  | 0.0  |
| 8.0-7.0  | 0.0  | 0.0  |
| 7.0-6.0  | 0.0  | 0.0  |
| 6.0-5.0  | 0.0  | 0.0  |
| 5.0-4.0  | 0.0  | 0.0  |
| 4.0-3.0  | 0.0  | 0.0  |
| 3.0-2.0  | 0.0  | 0.0  |
| 2.0-1.0  | 0.0  | 0.0  |
| 1.0-0.0  | 0.0  | 0.0  |

• DISTRIBUTION GRAPH (BY VOL.)



C2 PSDS

1) C2 MILL PASS II

2) C2 + PASS III of 1/2 of ①

③ C2 MILL PASS IV<sup>⊗</sup> of other 1/2 of ①

④ fines from ①, ②, ③ III

⊗ 3<sup>rd</sup> MILLING PASS ineffective due to clogged bag  
& powder charged channels

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and  
by

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36  $\text{SrTiO}_3$  3/4 Synthesis (see Book III page 77 for work-up)  
 No comp  $\rightarrow$  698, 39's

Prep:

|                 |          |               |
|-----------------|----------|---------------|
| tare            | 206.15   |               |
| $\text{SrCO}_3$ | 50.00 g  | desired       |
|                 | 256.15   |               |
|                 | 256.15/6 | actual wght   |
|                 | 0.0      | $\Delta$      |
| $\text{TiO}_2$  | 27.062   | desired       |
|                 | 283.212  | desired       |
|                 | 283.22   | actual wght   |
|                 | +0.01    | $\Delta$      |
|                 | +0.01    | scale replace |
|                 | ~0.0     | $\Delta$ net  |

1 hr<sup>+</sup> mixing

Transfer

|      |                    |               |
|------|--------------------|---------------|
| tare | 89.20              |               |
|      | 166.23             | final wght    |
|      | 77.03 <sup>+</sup> |               |
|      | 77.062             | expected      |
|      | -0.03 g            | $\Delta$ 0.04 |

|         |                           |
|---------|---------------------------|
| 185.56  | total prelim. wght of top |
| 19.33 g | top                       |

|                      |        |           |
|----------------------|--------|-----------|
| theoretical expected | 151.36 | w/out top |
|                      | 19.33  |           |
|                      | 170.69 | w/ top    |

3/5  
 150.97

14.87 + 62.16 = 77.03 ~ correct

Ramp @ 700C/hr to 1450C  $\Rightarrow$  to temp ~ 3:25

0.39/150.97 (0.258% loss)

GROUND yield  $\Rightarrow$  61.39/62.16  $\Rightarrow$  98.8%  
 ~1% grinding loss

Clean X-RAY. M.O.D. 1 HOUR.

Syn PROJECT COMPLETE  
 3/5

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3/4/88

C2 pellets

C2P12-15, IBM Technical Notebook  
 C2P16-17, Intel 1 mill III  
 2 IV

3700/27000

37

C2P12 3.075 0.572 0.191  
 3/21 → (3.08) 1.453 0.485 0.804  
 page 44

3.825 60.0

C2P13 3.02 0.573 0.188  
 3/21 → (3.02) 1.455 0.477(5) 0.794  
 page 44

3.803(5) 59.7

C2P14 3.11 0.574 0.192(3)  
 page 47 1.458 0.488 0.815

3.82 59.9

C2P15 3.11 0.574(5) 0.192(3)  
 page 47 1.459 0.488 0.816

59.8

C2P<sup>2</sup>16 3.25 0.573 0.202  
 1.455 0.513 0.853

59.8

C2P<sup>2</sup>17 3.22<sup>add 0.02</sup> 0.573 0.202  
 SR chipped (3.24) del 1.455 0.513 0.853

59.6<sup>+</sup>

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# 38 SrTiO<sub>3</sub> GB Doping IBM Technical Notebook

10g SrTiO<sub>3</sub> w/ 2 wt % B<sub>2</sub>O<sub>3</sub> added

Sp. g - 8.8 m.p. 820°C

10g + 0.2g B<sub>2</sub>O<sub>3</sub> ⇒ 10.2

0.2g A<sub>2</sub>O 7.14g/cc Decomposes above 300°C

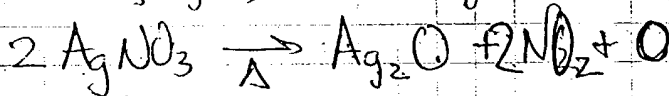
AgNO<sub>3</sub> ⇒ mp 212°C bp ⇒ decomp 169.8749 mw

4.328g/cc

0.2g Ag<sub>2</sub>O ×  $\frac{231.7394}{169.8749} \frac{\text{AgNO}_3}{\text{g Ag}_2\text{O}}$  ⇒ 0.733, 1.364

0.2g Ag<sub>2</sub>O ×  $\frac{169.8749}{231.7394} \frac{\text{Ag}_2\text{O}}{\text{g AgNO}_3}$  = 0.1466 ≈ 0.15g  
 X2 = 0.29

0.2g AgNO<sub>3</sub> × 169.874g



~~0.2g Ag<sub>2</sub>O ×  $\frac{231.7394}{169.8749} \frac{\text{Ag}_2\text{O}}{\text{g AgNO}_3}$  = 0.278g AgNO<sub>3</sub>~~

3.20, 3.13, 3.92  
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I27500 Doped ST<sub>2</sub>O<sub>3</sub> pellets

STA-1 3.10 0.581 0.196  
1.476 0.498  
3.0 0.525 0.178  
1.333 0.452

STA-3 deformed, ST<sub>2</sub>O<sub>3</sub> basis  
3.64 75.7  
0.852  
4.75 98.8  
0.632

Free 3/5 39

STA-2 3.25 0.581 0.208  
1.476 0.521  
3.14 0.525 0.185  
1.334 0.470

3.65 75.9  
0.891  
4.78 99.1 ← polish

I24

STB-1 3.03 0.587 0.191  
1.491 0.485  
2.88 ← 2.72 0.590 0.171  
(chip) 1.370 0.437

3.58 74.4  
0.847 4.47 92.9  
0.644

STB-2 3.17 0.586 0.197  
1.488 0.500  
3.03 ← 3.21 0.179  
1.370 0.455

3.645 75.9  
0.869(5) 4.52 94.  
0.671

I27500

STB-3 3.77 0.583 0.237  
1.481 0.60  
3.61 ← 3.74 0.534 0.216  
deformed 1.356 0.549

3.66 76.1  
1.03 4.55 94.6 ← polish  
0.773

ST-D1 3.62 0.585 0.235 <sup>new</sup>  
1.486 0.597  
3.60 ← 3.67 0.527 0.210  
1.339 0.533

1.03(5) 3.50 72.8  
4.77 99.2 ← polish  
0.7505

Comments - green D<sup>c</sup> fairly consistent, even w/ pressure variation

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DD-X 37/22000  
 2.88 0.573 0.169 4.04 63.4%  
 1.455 0.429 0.713  
 2.83 0.508 0.144  
 1.290 0.366 0.478  
 93

DD-Y 2.99 0.575 0.174 4.04 63.4%  
 1.46(5) 0.442 0.740(5)  
 2.93 0.509 0.149  
 1.293 0.379 0.498  
 92.4

10°C/MIN RAMP IN NEW  $Al_2O_3$  CRUCIBLE ON FRESH DD POWDR.  
 975°C for 2 HOURS } QUENCH. 20 MIN  $O_2$  PURGE.

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Date \_\_\_\_\_

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41

NOPIEF CAPA-See  
 PARTICLE ANALYZER

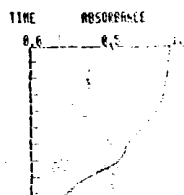
DATE 2/24/88  
 SAMPLE 2/24/88  
 SOLVENT ISO

## • CONDITIONS

SOLV. VISC 2.79 (CP)  
 SOLV. DENS 6.79 (G/CC)  
 SAMP. DENS 0.86 (G/CC)  
 D(CMAX) 10.0 (PP)  
 D(CMIN) 1.00 (PP)  
 D(CDIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 0 SEC

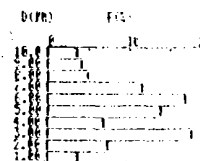
## • DATA



## • DISTRIBUTION TABLE (BY VOL.)

| D (PP)     | F (G)     | F (G) |
|------------|-----------|-------|
| 10.0 - 9.0 | 10.0      | 10.0  |
| 9.0 - 8.0  | 3.5       | 12.5  |
| 8.0 - 7.0  | 4.0       | 22.5  |
| 7.0 - 6.0  | 11.0      | 34.5  |
| 6.0 - 5.0  | 16.0      | 50.5  |
| 5.0 - 4.0  | 12.0      | 64.5  |
| 4.0 - 3.0  | 6.0       | 71.5  |
| 3.0 - 2.0  | 17.0      | 88.5  |
| 2.0 - 1.0  | 7.0       | 95.5  |
| 1.0 - 0.0  | 3.0       | 100.0 |
| D (AVE)    | 5.00 (PP) |       |

## • DISTRIBUTION GRAPH (BY VOL.)



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 PARTICLE ANALYZER

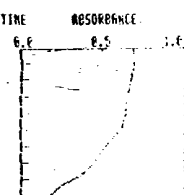
DATE 2/24/88  
 SAMPLE 2/24/88  
 SOLVENT ISO

## • CONDITIONS

SOLV. VISC 2.79 (CP)  
 SOLV. DENS 6.79 (G/CC)  
 SAMP. DENS 0.86 (G/CC)  
 D(CMAX) 10.0 (PP)  
 D(CMIN) 1.00 (PP)  
 D(CDIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 0 SEC

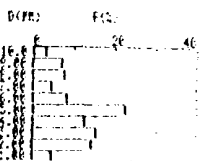
## • DATA



## • DISTRIBUTION TABLE (BY VOL.)

| D (PP)     | F (G)     | F (G) |
|------------|-----------|-------|
| 10.0 - 9.0 | 0.0       | 0.0   |
| 9.0 - 8.0  | 2.5       | 2.5   |
| 8.0 - 7.0  | 7.1       | 10.0  |
| 7.0 - 6.0  | 7.0       | 17.1  |
| 6.0 - 5.0  | 4.0       | 21.1  |
| 5.0 - 4.0  | 0.3       | 30.4  |
| 4.0 - 3.0  | 22.0      | 52.4  |
| 3.0 - 2.0  | 12.0      | 64.4  |
| 2.0 - 1.0  | 15.5      | 80.0  |
| 1.0 - 0.0  | 14.5      | 94.5  |
| 1.0 - 0.0  | 4.5       | 100.0 |
| D (AVE)    | 4.12 (PP) |       |

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 PARTICLE ANALYZER

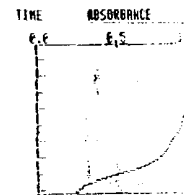
DATE 2/24/88  
 SAMPLE 2/24/88  
 SOLVENT ISO

## • CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 6.79 (G/CC)  
 SAMP. DENS 0.36 (G/CC)  
 D(CMAX) 10.0 (PP)  
 D(CMIN) 1.00 (PP)  
 D(CDIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 20 SEC

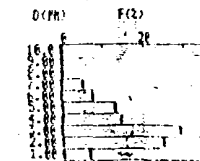
## • DATA



## • DISTRIBUTION TABLE (BY VOL.)

| D (PP)     | F (G)     | F (G) |
|------------|-----------|-------|
| 10.0 - 9.0 | 0.0       | 0.0   |
| 9.0 - 8.0  | 0.0       | 0.0   |
| 8.0 - 7.0  | 0.0       | 0.0   |
| 7.0 - 6.0  | 0.0       | 0.0   |
| 6.0 - 5.0  | 5.1       | 5.1   |
| 5.0 - 4.0  | 7.0       | 12.1  |
| 4.0 - 3.0  | 12.0      | 24.1  |
| 3.0 - 2.0  | 14.0      | 38.1  |
| 2.0 - 1.0  | 29.0      | 67.1  |
| 1.0 - 0.0  | 24.0      | 91.1  |
| 1.0 - 0.0  | 6.0       | 100.0 |
| D (AVE)    | 2.05 (PP) |       |

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3/15 DC batch II ST-103

per ton 206.11 (206, unstable  
 $\frac{256.06(7)}{49.99 \text{ g}}$  loss 0.05 (0.1%) desired 50g

$\frac{27.06 \cdot 2}{283.122}$  target  
 $\frac{283.13}{27.07}$  actual ✓  
 $\frac{77.02}{+0.008}$  total

$\frac{88.34(5)}{77.02}$  Pt curr tone  
 $\frac{165.36(7)}{165.34}$  total above  
 expected comb. wght  
 0.03 g error max, ✓ OK. (0.04% error)

~184.54 (19.20 tone) ✓ expect ~154.0 w/out top

~~10.03~~ 150.15 after cooling!

3/16 4.20 < 100 mesh 59.85 g

ST-D2 (2.9mm) M.II  
 $\frac{3750}{3.04}$  /25,000  

|       |       |       |       |
|-------|-------|-------|-------|
| 0.583 | 0.206 | 3.38  | 70.3% |
| 1.481 | 0.923 | 0.900 |       |
| 3.017 | 0.514 | 0.181 |       |
|       | 1.306 | 0.460 | 0.616 |
|       |       | 4.90  | 1.02% |

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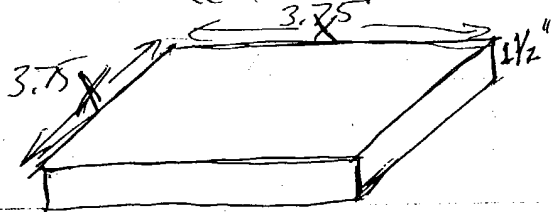
43

7070 GLASS count

1 1/2"

$$7070 \text{ density} - 2.13 \text{ g/cc} \Rightarrow \frac{\text{kg}}{1000 \text{ g}} \times \frac{0.00571 \text{ lbs}}{3.73 \times 10^{-4} \text{ kg}} \frac{\text{lbs}}{\text{cc}}$$

$$0.00571 \frac{\text{lbs}}{\text{cc}} \times \frac{16.387 \text{ cc}}{3.75 \text{ in}^3} = 0.0936 \frac{\text{lbs}}{\text{in}^3} \text{ Troy conv.}$$



$$0.08 \times 0.08 \times 1.5 = 21.32 \text{ in}^3$$

$$\frac{21.32}{24.9696} \times \frac{0.08001 \text{ lbs}}{\text{in}^3} = 1.997 \text{ lbs}$$

$$1.5 X^2 (0.08 \frac{\text{lbs}}{\text{in}^3}) = 2$$

$$1.5 (0.08 \text{ lbs/in}^3) X^2 = 2 \text{ lbs}$$

$$0.12 X^2 = 2 \text{ lbs}$$

$$X^2 = 16.66$$

$$X = 3.77 \text{ in}$$

check density conversion:  $2.13 \frac{\text{g}}{\text{cc}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ lb}}{3.73 \times 10^{-4} \text{ kg}} =$

$$\text{OK } \frac{0.00213 \text{ kg}}{\text{cc}} \times \frac{1 \text{ lb}}{0.4535 \text{ kg}} = 0.0048965 \frac{\text{lb}}{\text{cc}}$$

$$1 \text{ lb} = 4.535 \times 10^{-4} \text{ kg}$$

$$1 \text{ lb} = 0.435 \text{ kg}$$

$$0.0048965 \frac{\text{lb}}{\text{cc}} \times \frac{16.387 \text{ cc}}{\text{in}^3} = 0.08 \frac{\text{lbs}}{\text{in}^3}$$

4 X 4 X 1.5 OR 5 X 5 X 1

@ 1" thick  $0.08 X^2 = 2$   
 $X^2 = 25$   
 $X = 5$

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IBM Technical Notebook

3/21 1<sup>st</sup> pellet 700C for 12 hrs → START @ 3 to ramp @ 10°/min to 700C for 16-17 hrs.  
 C2P12 for green data on all pellets see pg 37  
 C2PB 2<sup>nd</sup> pellet 750C data to run concurrently

Peter,

Since we didn't get to discuss this experiment in more detail, here is what needs to happen.

5 pellets - C2 overnight Int.  
 1<sup>st</sup>) - 700° C ~12 hr O<sub>2</sub> 308  
 2<sup>nd</sup>) - 750° C ~12 hr O<sub>2</sub> 302  
 3<sup>rd</sup>) - 800° C " " "  
 4<sup>th</sup>) - 850° C " " "

After three intermediate temperature anneal, weigh and measure each pellet. If no sintering, or at least a negligible amount, has occurred, then re-fire each sample for 12 hrs again at the same intermediate temperature and then sinter each pellet for 2 hrs at 950° C. Ramp from the intermediate T to 950° fast (~20°/min).

} 965C used

Also sinter the 5<sup>th</sup> pellet at 950° C for 2 hrs, this is the control pellet. Thanks and have a good week.

P. Vane

3/21-9:00 AM 17 HRS

C2P12 3.06 (Δ-0.02) 0.572 0.191 no sintering, but 0.65% wght loss  
 3.01 0.50 0.163 5.65 88.7  
 1.27 0.414 0.533 CRACKING - closing

C2P13 3.01 (Δ-0.05) 0.572 0.187 no sintering, but 0.60% wght loss  
 2.97 0.504 0.163 5.57 87.4  
 1.280 0.414 0.533 NO CRACKING - open

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3/21  $\text{SrTiO}_3$  DRC-batch 2  $\rightarrow$  fine coll after 3<sup>rd</sup> milling  $\rightarrow$  11g yield  
 after cleaning ~ 2g loss to machine  
 3g loss to blow-out  
 fines  $\rightarrow$  1.34  $\mu\text{m}$  ave  
 medium III  $\rightarrow$   $\geq$  2.2  $\mu\text{m}$  range (2.2-2.8)  
 approx. { 18% fines  
 expectations { 82% medium  
 + 50g medium  
 61g / 72 avg.  
 ~ 85% yield

STDX1f-1 0.570 0.212 3.09 64.2% {versus 72 on 3um probes}  
 2.74 1.448 0.538(5) 0.887

In furnace ~ 3:00 p.m., tripped off @ 975 2X, cooled to 1400C, then to 1600C.

Temp recovered/reset to 1650 @ 4:30 p.m.

3/22 RAN all nite! 24 hrs @ 3:00 p.m. Tuesday, 42 HRS @ 9:00 AM WEDS.  
 2.70 0.487 0.178 4.97 1.033% same as 2/2's  
 1.237 0.452 0.543

Keter:

✓ start Cut, section and polish Cu-Bi slab (Start Plan) start/finish 21/22

• Try firing one pellet of  $\text{SrTiO}_3$  to 1350C as is

• Try slip casting a pellet of  $\text{SrTiO}_3$

$\rightarrow$  SwinJet mill  $\text{SrTiO}_3$  powder down to ~ 1  $\mu\text{m}$ . The mill require "tuning" the jet mill. Run for 1600C overnight

✓ • Make master batch of  $\text{SrTiO}_3$ ?

tare 202.33 \* approx. due to instability spans close: sometimes stable  
 60.00  
 252.33 target  
 act wght 252.33 \*  $\checkmark$   
 27.062  
 279.392  
 act weight 279.4 ~ 0.01

TRANSFER. 165.22 act wght  
 tare 88.17  
 77.05 wght mix  
 77.07 expected  
 ~ 0.03% loss  
 POST/16HR 150.02  
 + 14.87 g ~ expected loss  
 164.89  
 150.2g actual loss



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write up 3/23, powder 3/24 morning

# IBM Technical Notebook

46/3/22 C3-Synthesis  
 (Reference)

Synthesis  
 $\text{BaCO}_3$

tape  $\rightarrow 277.72$  to zero  
 weight: ?

3/23  $\frac{398.24-6}{120.52-54} (-0.02\%)$

$\text{CaO}$

tape  $\rightarrow 0.89 \rightarrow$  zeroed  
 weight:  $72.58 (7/9)$  3/23

transfused quant

$\text{CaO}_3$

tape  $\cdot 0.85 \rightarrow 2.5$  3/23  
 weight  $34.35$

total expected  $\Rightarrow 227.46$   
 transfused quant,  $+0.03\%$

Overwrite @ 70C in 30" vacuum after "bump-free" isopropanol mixing  
 3/24  $\frac{230.56}{116.57} \frac{230.41}{117.17}$   
 $\frac{113.99}{113.99} + \frac{113.24}{113.24} \Rightarrow 227.23 \cdot 0.1\% \text{ loss or}$

Prior to removing from bkr after overwrite, cake broken up and  
 "pulverized", then let cool under vacuum to remove any sol. resid.

In Surface @ 12:30 500C/HR RAMPS, 955 RXNT in flowing oxygen  
 3/25  $\frac{219.22}{102.65} \frac{218.34}{101.17} \Rightarrow \frac{203.82}{202.13} 0.83\% \text{ loss}$   
 $218.36$

14 C2 Batch  $\rightarrow \frac{1}{2} \text{BaCO}_3 \cdot \text{O}_2$  200g

From C1 batch calc. (99.94 Batch 100) 72.58 (7/9)

$\text{CaO} \Rightarrow 17.1535 \rightarrow 17.1907 \rightarrow \times 2 \Rightarrow 34.34$

$\text{BaO}_x \Rightarrow 46.5939 \cdot 100 \Rightarrow \times 2 \Rightarrow 93.1868$

$\text{BaCO}_3 \text{ counterflow: } 93.1868 \frac{137.35}{133.34} = 119.932(1) \div 0.99 \Rightarrow 121.14(9)$

$\text{CaO} \Rightarrow 36.25(1) \Rightarrow 36.2595(1) \Rightarrow \times 2 \Rightarrow 72.51(9)$

OK. everything is Ba rich by analysis, so okay not correct  $\rightarrow 119.93$   
 Apply 1/2.  $\text{BaCO}_3$   $\frac{120.52}{120.52} \Rightarrow 120.52$

tape:  $\frac{277.67}{120.52} \frac{400.21}{400.21}$  won't need bit will fare

reads:  $120.57(6-6)$  ooo 4/5

tape:  $0.89/77$   $72.58$  transfused quant. low to zero paper

4/13 transfused quant  
 paper under 0.1 after checked due to chiller flow change  
 not off of glass/dry removal 0.00. Thick OK then  
 it spilled glove till (not sure how 0.3% error)  
 34.34/5  $\frac{227.46}{227.46}$  3 day

$\text{BaO} \cdot 5.72 \text{ g/kc}$   $\text{BaCO}_3 \cdot 4.43$   $\text{CaO} \cdot 5.01$   $\text{CO} \cdot 6.5-6.49$   
 $\therefore$  if pumping occurs w/ selective loss  $\text{BaCO}_3$  should preferentially be  
 lost  $\rightarrow$  not  $\rightarrow$  uniformity suspended.

The above understood  
 and witnessed by

Date

and  
 by

3/8.71

Date

3/23 from pg 44 <sup>IBM Technical Notebook</sup> TREATMENT INQUIRY

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C2P14 & C2P15 ⇒ original green & info on pg 37; both 3.11 then now

C2P14: (800°C pretreat), purge - 2120 p.m. 59.9 ad. : 18 HRS  
 3.09 0.573 0.191 3.83 60.1 no appreciable sintering  
 1.455 0.485 0.806  
 3.07 0.522 0.171 5.125 80.5 apparently sintering  
 1.326 0.434 0.599 appreciable

C2P15: (850°C pretreat) purge as above - 59.8 ad. : 18 HRS  
 3.09 0.565 0.187 4.02 63.1 slight amount of sintering  
 1.435 0.475 0.768  
 3.08 0.531 0.174 4.87 76.5% initial sintering "appreciable"  
 1.319 0.442 0.632

C2P18 (CONTROL) 37/27500  
 2.92 0.574 0.180 3.83 60.1% O.K.  
 1.458 0.457 0.763  
 2.86 0.501 0.152 5.82 91.4 ⚡  
 3/28 1.273 0.386 0.491  
 Post 48 hr (2<sup>nd</sup> 24) - C3 batch

pre → 318.71  
 post → 316.88  
 (-) 1.83  
702.13  
 200.30  
199.23 initial prod. yield

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48/23 from page 45 IBM Technical Notebook

STD-4f grain size slightly larger - interior fairly uniform  
~25  $\mu$ m ave by occasional

~~Re-sinter~~ Re-sintered overite to check for additional growth.  
Further polishing of 40 hr sample slice yields numerous 40-50  $\mu$ m  
GRAINS! Growth seems predictable!

3/24 Summary from 45  
Green 2.74 1.448 0.538(5) 0.887 3.09 64.2  
4218 @ 2.70 1.237 0.452 0.543 4.97 100.33  
1645C

slice back up to 1650 @ 5:00 PM (4 hr earlier due to control couple failure)  
63 HRS SHUT OFF @ 1:45 PM 3/24 (421 hr)

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3/24 from pg 45

after additional 12 hr rxn time  $\frac{150.02}{149.81}$  Assume constant vol  
 $\sim 0.21 g$   
 total loss: 165.22 initial  $\Delta$   
 150.02 16 HR - 15.20 98.6% reacted  
 149.81 28 HR - .21 1.4%  
 15.41

CASE FOR MINOR porosity?

- > 61 gs recovered after mortar grinding.
- > 2 HRS on shaker mill w/ 5mm balls.
- > 60.4 g shaker yield
- > 18.8 g MI JET YIELD

PSD  
 2.91  $\mu m$  ave.  $\Delta$  flatter than jet, but not much better  $\phi$  size.

Slip-cast calculations: die 0.9" id.  $\Rightarrow 2.286 cm$  0.762 cm  
 0.3" desired green thickness  
 $\frac{\pi (2.286)^2}{4} (0.762) = 3.1275 cc (1.81 g/cc) = 15 g SrTiO_3 (0.6) = 9.0g$   
 approx density

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NORIBA CAPA-500  
 PARTICLE ANALYZER

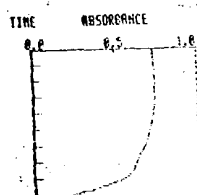
DATE 3/2/88  
 SAMPLE S-103-1882  
 SOLVENT 150  
 MIT

## • CONDITIONS

SOLV. VISC 2.10(CP)  
 SOLV. DENS 0.79(G/CC)  
 SAMP. DENS 4.81(G/CC)  
 D(MAX) 10.0 (PM)  
 D(MIN) 1.00(PM)  
 D(DIV) 1.00(PM)  
 SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

## • DATA

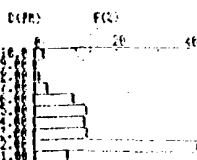


## • DISTRIBUTION TABLE (BY VOL.)

| D(PH)     | F(1) | F(2)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 1.0  | 1.0   |
| 9.00-8.00 | 0.0  | 1.0   |
| 8.00-7.00 | 1.0  | 2.0   |
| 7.00-6.00 | 2.9  | 5.7   |
| 6.00-5.00 | 9.5  | 15.2  |
| 5.00-4.00 | 12.5 | 27.6  |
| 4.00-3.00 | 12.1 | 35.8  |
| 3.00-2.00 | 12.6 | 50.6  |
| 2.00-1.00 | 35.6 | 52.1  |
| 1.00-0.00 | 7.9  | 100.0 |

D(AVE) 2.20 (PM)

## • DISTRIBUTION GRAPH (BY VOL.)



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 PARTICLE ANALYZER

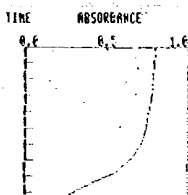
DATE 3/2/88  
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 D(MIN) 1.00(PM)  
 D(DIV) 1.00(PM)  
 SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

## • DATA

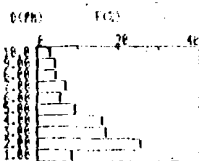


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| D(PH)     | F(1) | F(2)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 1.1  | 1.1   |
| 9.00-8.00 | 4.2  | 7.3   |
| 8.00-7.00 | 4.5  | 11.5  |
| 7.00-6.00 | 6.9  | 18.8  |
| 6.00-5.00 | 5.4  | 24.2  |
| 5.00-4.00 | 9.2  | 33.4  |
| 4.00-3.00 | 16.6 | 45.4  |
| 3.00-2.00 | 17.0 | 60.2  |
| 2.00-1.00 | 25.2 | 81.6  |
| 1.00-0.00 | 6.4  | 100.0 |

D(AVE) 2.55 (PM)

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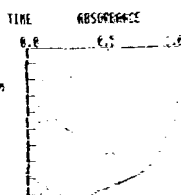
DATE 3/2/88  
 SAMPLE S-103-1882  
 SOLVENT 150  
 MIT

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 SAMP. DENS 4.81(G/CC)  
 D(MAX) 10.0 (PM)  
 D(MIN) 1.00(PM)  
 D(DIV) 1.00(PM)  
 SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

## • DATA

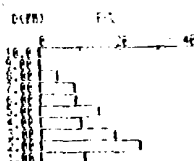


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| D(PH)     | F(1) | F(2)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 0.0  | 0.0   |
| 9.00-8.00 | 0.0  | 0.0   |
| 8.00-7.00 | 4.7  | 4.7   |
| 7.00-6.00 | 8.4  | 12.5  |
| 6.00-5.00 | 8.7  | 21.6  |
| 5.00-4.00 | 14.4 | 26.1  |
| 4.00-3.00 | 5.5  | 45.3  |
| 3.00-2.00 | 10.4 | 64.7  |
| 2.00-1.00 | 24.9 | 89.2  |
| 1.00-0.00 | 16.7 | 100.0 |

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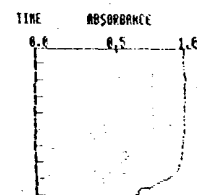
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 SAMPLE S-103-1882  
 SOLVENT 150  
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 SOLV. DENS 0.79(G/CC)  
 SAMP. DENS 4.81(G/CC)  
 D(MAX) 10.0 (PM)  
 D(MIN) 1.00(PM)  
 D(DIV) 1.00(PM)  
 SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

## • DATA

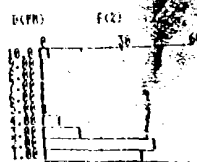


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| D(PH)     | F(1) | F(2)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 2.9  | 2.9   |
| 9.00-8.00 | 0.0  | 2.9   |
| 8.00-7.00 | 0.0  | 2.9   |
| 7.00-6.00 | 0.0  | 2.9   |
| 6.00-5.00 | 0.0  | 2.9   |
| 5.00-4.00 | 0.0  | 3.8   |
| 4.00-3.00 | 5.9  | 9.6   |
| 3.00-2.00 | 15.4 | 23.8  |
| 2.00-1.00 | 41.0 | 64.7  |
| 1.00-0.00 | 35.9 | 100.0 |

D(AVE) 1.34 (PM)

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IBM Technical Notebook

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3/20

10g  $\text{SrCO}_3 \Rightarrow 0.06774$  moles  
5.412g  $\text{TiO}_2$

15.412g total

15.48 after mixing recovery

2/25/93 Note  
Density calculations here were done using Pycnometer which is now known to be in error. It is 5.116 not 4.82

Dave's unreacted  $\text{SrCO}_3/\text{TiO}_2$  { new batch  $\text{SrTiO}_3$

2.975 0.584 0.242

2.42 0.458 0.190  
1.16 0.483 0.510

2.91 0.585 0.194

2.90 0.482 0.173  
1.326 0.439 0.606

4.745

98.6

NOT TOO GOOD

4.785

99.5

NOT TOO GOOD

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52.4/1  $\text{SrTiO}_3$  grow growth IBM Technical Notebook

pellet 2 of fines

|      |       |       |       |
|------|-------|-------|-------|
| 2.22 | 0.572 | 0.169 | 3.12  |
|      | 1.453 | 0.429 | 0.711 |
| 2.19 | 0.487 | 0.144 | 4.98  |
|      | 1.237 | 0.366 | 0.440 |

64.9% ~ same as before

10035% = 103.5

1470C

|              |       |       |       |
|--------------|-------|-------|-------|
| 2.71         | 0.580 | 0.176 | 3.76  |
| Davis excess | 1.473 | 0.447 | 0.762 |

74.0%

$\text{TiO}_2$   
 estimate on 1/2 0.518 (0.262) 0.160  
 et. 35 1.32 0.406 0.556  
 (2.70) ~~1.32~~ ~~0.406~~

4.86 → 1.01

101. -

~ O.K. by wght.

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# IBM Technical Notebook

M.W.

5.3

~~SrTiO<sub>3</sub> doping~~  
~~1/2 mole % SrTiO<sub>3</sub>~~

SrCO<sub>3</sub>

Al<sub>2</sub>O<sub>3</sub>

V<sub>2</sub>O<sub>5</sub>

SrTiO<sub>3</sub>

0.0676 <sup>x2</sup> 0.135225g batches

0.125 0.25

STOIC as nitrate  
 0.086 ~~SAUC~~

0.154 0.308

79.90

0.0676

147.63

101.96

181.88 3357 690C

183.5182

13.531 TiO<sub>2</sub> 0.16935 moles 0.00084675 = 1/2 mole %  
 25.00 SrCO<sub>3</sub>  
 38.531

0.00084675 moles (79.90) - 0.06766 + 13.531 = 13.46

0.00084675 (147.63) - 0.125 + 25. = 24.875

Summary of additions, quantities

|                                     | excess             | SUB 1  | SUB 2          | excess 2 |
|-------------------------------------|--------------------|--------|----------------|----------|
| TiO <sub>2</sub> (x2)               | 13.5986<br>13.6662 | 13.443 | 13.531         | 13.531   |
| SrCO <sub>3</sub> (x2)              | 25.00              | 25.00  | 24.846         | 25.246   |
| Al <sub>2</sub> O <sub>3</sub> (x2) | -                  | 0.086* | -              | -        |
| V <sub>2</sub> O <sub>5</sub>       | -                  | -      | 0.154*<br>0.16 | -        |

\* these quant's are x2 since there are 2 moles of Al { V in Al<sub>2</sub>O<sub>3</sub> } V<sub>2</sub>O<sub>5</sub>

Correction:  $\frac{0.16}{147.63} = 0.00108$  moles SrCO<sub>3</sub>

$\frac{0.00108 \text{ moles}}{0.00169}$  { 64% with loss due to decanting approx  
 70% stoic or 30% off addition excess  
 V<sub>2</sub>O<sub>5</sub> }

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54 4/5

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Sub2  $\text{V}_2\text{O}_5$  1 mol % stoichiometric / not excess (see pg 53)

25.0 g  $\text{SrCO}_3$  weighed & transferred to beaker  
 0.16 g removed  
 0.16 g  $\text{V}_2\text{O}_5$  added (saturated in hot water, decont.)

MISTAKE, now uncorrectable. Should have been:

$$0.00084675 (2) = 0.0016935 \text{ g } \text{SrCO}_3 \text{ removed}$$

$0.0016935 (147.63) = 0.25 \text{ g}$  however, deconting over residual pack reduced actual  $\text{V}_2\text{O}_5$  addition, and though NONSTOICHIOMETRIC (slightly) will use to see what happens.

38.02 g yield after overwite vac @ ~90°C  
 38.53 initial  
 0.51 loss in mixing 1.3 %

38.88 tare (zeroed)  
 38.08 466 extra due to final beaker scrape ✓

In furnace to temp by 12:00, 4/6/88 16 HRS 8 A.M 4/7

'Severe' sintering, dark black appearance of pack body

126.96  
 117.68  
 ~0.05 g spillage  
 117.73

$$25 \text{ g } \text{SrCO}_3 \times \frac{103.62}{147.63} = 17.55$$

$$\begin{array}{r} 126.96 \\ - 117.68 \\ \hline 9.28 \end{array}$$

~7.40 g expected loss

! some bound water?

26.18 g ground yield

See 57 & 58  
 FOR SINTERED

IBM Technical Notebook

Sub 1 ~~Al<sub>2</sub>O<sub>3</sub>~~ → 1 mole % added as nitrate

$$0.00084675(2) = 0.0016935 \text{ moles} // \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} \quad 375.14$$

$\downarrow$  1/2 mole %      1 mole %      Al 1:1 so use 0.0016935 moles

$$0.0016935 \text{ moles Al nitrate} \left( \frac{375.14 \text{ g}}{\text{mole}} \right) = 0.6353 \text{ g}$$

(303172)

So remove 0.0016935 moles TiO<sub>2</sub> ∴ 0.0016935(79.9) = 0.135 g TiO<sub>2</sub>

$$13.531 - 0.135 = 13.396 \text{ g TiO}_2, 0.6353 \text{ g Al nitrate in soln}$$

$$\begin{array}{r} 38.29 \text{ mix yield} \\ 39.03 \text{ theoretical} \\ \hline 0.74 \text{ mix loss} \end{array}$$

1.9%

$$0.6353 \text{ g} \left( \frac{101.9612}{375.14} \right) = 0.173 - \Delta 0.46$$

$$\begin{array}{r} 39.03 \\ - 0.46 \\ \hline 38.57 \end{array}$$

87.55 tare (zeroed)  
38.27 note: nitrate decomposes in hot water. Must explain some of loss

In furnace to temp by 12:00 p.m., 4/6/88 → 16 hrs 8 am 4/7  
little sintering of powder, light SrTiO<sub>3</sub> color, mottled.

$$\begin{array}{r} 118.54 \\ 127.82 \\ \hline - 9.28 \text{ g} \end{array}$$

same as SUB 2! but giving the same, even though exact loss is coincidence.

yield → 27 g

see 57/58  
for SINTERED DATA

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# IBM Technical Notebook

Two Oxides

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Figs. 296-301

Phase Diagrams  
 (arrows)  
 for  $\text{SrO} \cdot \text{TiO}_2$   
 system, and  
 assorted others

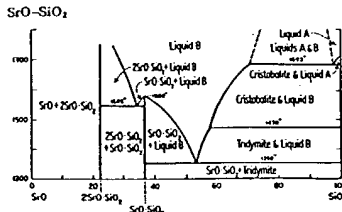


FIG. 296.—System  $\text{SrO-SiO}_2$ .

P. Eskola, *Am. J. Sci.*, 5th Ser., 4, 336 (1922); modified by J. W. Greig, *ibid.*, 5th Ser., 13, 19 (1927); see also F. C. Krueck, *J. Am. Chem. Soc.*, 52 [4] 1440 (1930).

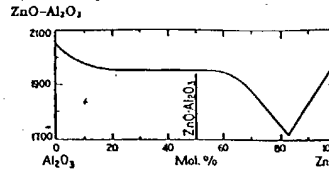


FIG. 299.—Liquidus curve of system  $\text{ZnO-Al}_2\text{O}_3$ .

E. N. Bunting, *Bur. Standards J. Research*, 8 [2] 280 (1932); R. P. 413.

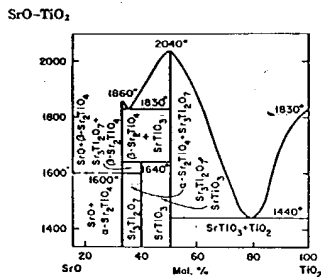


FIG. 297.—System  $\text{SrO-TiO}_2$ .

Miroslawa Dryl and Włodzimierz Trzebiatowski, *Roczniki Chem.*, 31, 492 (1957).

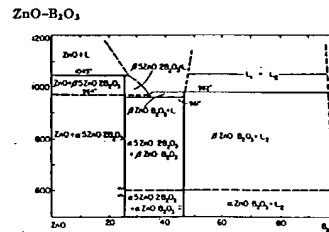


FIG. 300.—System  $\text{ZnO-B}_2\text{O}_3$ .

D. E. Harrison and F. A. Hummel, *J. Electrochem. Soc.*, 103 [9] 496 (1956); see also, "Structure of Zinc Metaborate,  $\text{Zn}_2\text{O}_3(\text{BO}_3)_2$ ," P. Smith, S. Garcia-Blanco, and L. Revoit, *Anales Real Soc. Espan. Fis. Quim. (Madrid) Ser. A* (Nov.-Dec.), 263-268 (1961).

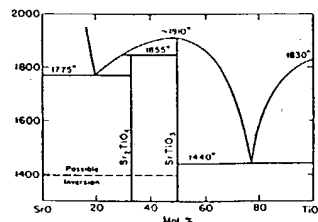


FIG. 298.—System  $\text{SrO-TiO}_2$ ; tentative.  
 Rustum Roy; private communication, 1957.

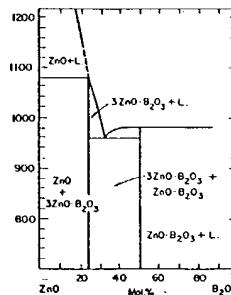


FIG. 301.—System  $\text{ZnO-B}_2\text{O}_3$ .

Va. S. Leonov, *Zhur. Neorg. Khim.*, 3, 1246 (1958).

Two Oxides

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Figs. 2334-2336

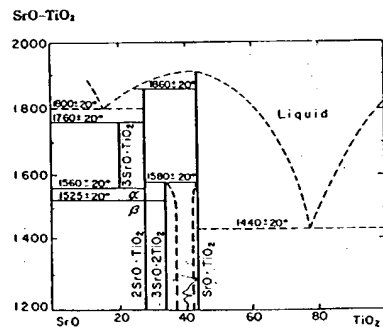


FIG. 2334.—System  $\text{SrO-TiO}_2$ .  $2\text{SrO} \cdot \text{TiO}_2$  is extends to approximately the  $4\text{SrO} \cdot 3\text{TiO}_2$  composition.

Antonio Cocco and Franco Mazzuca, *Ann. Chim. (Rome)*, 53, 802 (1963).

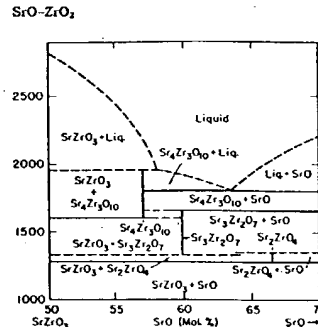


FIG. 2335.—System  $\text{SrO-SrZrO}_3$ .

Gilbert Tilloy and Monique Perez y Jorba, *Rev. Hautes Temp. Refractaires*, 1 [4] 337 (1964).

The above understood

Date

and

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sibly important  
sure of

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Excess  $\text{SrTiO}_3$

(Excess 2) IBM Technical Notebook

(Excess 1)

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13.531  $\text{TiO}_2$   
13.53-  
zero off after addition  
probably static

25.25  $\text{SrCO}_3$   
25.28

13.6  $\text{TiO}_2$   
13.61

25.00 Sr  
25.02  
.03 loss

In drying oven @ ~100C under house vacuum @ 1:30 p.m. 4/6/8

38.72 after drying  
87.87 weighed crucible  
126.59 w/ addition  
118.85  
7.74

38.43 after drying  
87.07  
125.50  
117.79  
7.71

$25 \times \frac{101.06}{375.14} = 6.775$  17.5

$\frac{6.775}{7.5} = 90.33\%$  12% excess loss  
 $7.5 / 7.7 = 97.5\%$

#1  $\leftarrow \text{TiO}_2$

#2  $\leftarrow \text{SrCO}_3$

NO GREEN DATA TAKEN

NO GREEN DATA

$\text{N}_2$   
2.75 0.520 0.159  
1.321 0.404 0.554  
2.71 0.529 0.160  
1.344 0.406 0.576

EXCHANGE  
3.01 0.517 0.175  
1.313 0.444(5) 0.60  
3.00 0.520 0.176  
1.321 0.447 0.613  
5.0 1.04  
4.89 1.02

$\text{SrCO}_3$   
2.38 0.540 0.135  
1.372 0.343 0.507  
 $\text{N}_2$   
2.41 0.554 0.141  
1.410 0.358 0.559

$\text{SrCO}_3$   
2.56 0.529 0.150  
1.314 0.381 0.5405  
2.60 0.526 0.151  
1.336 0.384 0.538  
4.74 98.5  
4.83 1.00

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SUBSTITUTION 1 :  $Al_2O_3$  1 mol % 16 HRS RXN.

" 2 :  $V_2O_5$  ↓

$N_2$   $O_2$

1 : 100.4 98.5

2 : 89.6 97.5

EXCESS DOPING 1 :  $\frac{1}{2}$  mol %  $TiO_2$

" 2 : ↓  $SrCO_3$

1 :  $N_2$   $O_2$

1 : 97.4 103

2 : 102 109

"MECHANICAL MANIPULATION"

finer : 103.4

finer  $\frac{1}{3}$ , med  $\frac{2}{3}$  mix : 102.3

MED : 100.4

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4/11 Phase C/Bi studies IBM Technical Notebook

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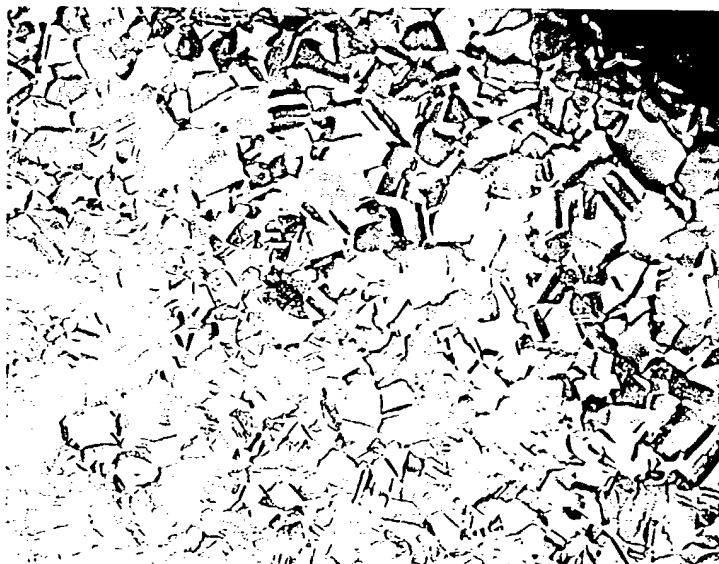
600C overnite  $N_2$  treatment on as rec'd material (Cu)



INTERIOR  
INHOMOGENEOUS  
(ABNORMAL)  
GRAIN GROWTH

100X

100  $\mu$ M



EXTERIOR  
HOMOGENEOUS

100  $\mu$ M

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and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

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IBM Technical Notebook

1, 3, 10% Bi in copper

5 g total per batch

4.95 post 750C

g Bi :  $5(0.01) = 0.05$      $5(0.03) = 0.15$      $5(0.10) = 0.5$  g

Cu                      4.95                      4.85                      4.50

actual                      0.05-6                      0.15-0.16                      0.50-1  
                                  4.95-6                      5.00                      4.99-5.0

recovery                      4.87 added to 5.00                      4.99 -                      4.95

~~5.00~~  
 4.98 after 400C over (not disturbed)                      4.90 after 400C over

Reloaded 1% & will continue w/ 3%. Will make a new 10%

And a 50% and fire @ 750C. Crucible shortage → will likely

modify Above.

50/50

2.5g Bi, 2.5g Cu

10% Bi

3% as above

g Bi: 2.51 actual

post Cu 5.01

Cu 2.40

cruc total  
 1.34  
6.34  
 5.00  
~~(4.99)~~

Post 750C

6.34  
 4.91

0.51  
5.02(3) total  
 4.51(2)

Post 750C

1.32(3)  
6.24  
 5.07 ?  
 4.92

6.21  
4.89

100% RESULT

{ NOTE: INITIAL 400C (420C) follow (1-10%) percentages of Bi  
 did not produce expected densification/solidification of peaks }

IBM Technical Notebook

25 { 35% Bi/Cu melts  $\frac{1}{2}$  1 Bi crucible filling  
 25%  
 $0.25(5) = 1.25 \text{ g Bi}, 3.75 \text{ Cu}$   
 $\begin{array}{r} 6.33 \\ 1.33 \\ \hline 5.00 \end{array}$  PRE  
 $\begin{array}{r} 1.75 \text{ Bi} ; 3.25 \text{ Cu} \\ 6.25(4) \text{ loaded} \\ 1.30(1) \\ \hline 4.95 \text{ starting total} \end{array}$

6.30 post  $\Delta = 0.03$   $\checkmark$   
 Possible post density: 0.315, 0.385  $\checkmark$   
 $\begin{array}{r} 4.97 \\ 0.800 \\ 0.978 \end{array}$  0.6 8.28 90.  
 definitely smaller volume, higher density  
 $\Delta = -0.02$

Argon/H<sub>2</sub> Bi filling

filled 12.82  
 cruc:  $\frac{11.39(40)}{11.49}$

CRUX  $\Rightarrow$

13.32 post  
 $\frac{13.31}{13.18}$  PRE  
 $\frac{11.86}{0.148}$

25%  
 1.26 Bi  
 5.03 w/Cu

post 12.81

13.30 after slag removal

Argon/H<sub>2</sub> 25% Bi Run  $\leftarrow$  Pellet Run  $\rightarrow$

pellet:  $\begin{array}{r} 4.87 \\ 1.232 \end{array}$   $\begin{array}{r} 0.485 \\ 0.564 \end{array}$   $\begin{array}{r} 0.222 \\ 0.672 \end{array}$  17.25 79%

$$8.96 \times 0.75 + 0.25(9.8) =$$

$$\frac{9.8}{6.72} + 2.45 = 9.17$$

Furnace started 2 HR purge 3.35"  
 4.84 0.483 0.234 " pellet bloating due to Bi vaporization?"

Bi<sub>2</sub>O<sub>3</sub>: sp. g. 8.8 m.p. 820°C



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IBM Technical Notebook

$\text{SnTiO}_3$  GRAM Growth Experiment - MECHANICAL MEASURES

- 1) PSD weighting
- 2) fines full density & free sintering of polished surface
- 3) reacted to constant weight (1st batch) sintering as in #2

SINES = F

|       |          |       |       |       |       |
|-------|----------|-------|-------|-------|-------|
| 2.004 | 0.570    | 0.155 |       | 3.14  | 65.3  |
|       | 1.498    | 0.394 | 0.649 |       |       |
| 2.01  | 0.988    | 0.132 |       | 4.975 | 10.34 |
|       | 1.239(5) | 0.335 | 0.409 |       |       |

fines/median = FM

|      |       |       |       |      |       |
|------|-------|-------|-------|------|-------|
| 2.19 | 0.577 | 0.154 |       | 3.32 | 69.0  |
|      | 1.465 | 0.391 | 0.659 |      |       |
| 2.17 | 0.504 | 0.135 |       | 4.92 | 102.3 |
|      | 1.28  | 0.343 | 0.441 |      |       |

chipped  $\mu$

|         |       |       |       |         |       |
|---------|-------|-------|-------|---------|-------|
| 2.46(7) | 0.582 | 0.165 |       | 3.43(5) | 71.4  |
|         | 1.478 | 0.419 | 0.719 |         |       |
| 2.46*   | 0.589 | 0.147 |       | 4.85    | 100.4 |
|         | 1.318 | 0.373 | 0.509 |         |       |

REMARKS: \* some powder adhered

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IBM Technical Notebook

4-12-88<sup>63</sup>

Sintering Regime

Rapid Temp w/ 10 cc/min O<sub>2</sub>

4:25 p.m.

1550C initial set, after REACHING temp for 1 HR, 1640C overnite

5:20 p.m. ~ 1100C, T<sub>control</sub> blown. o. ~ 30-45 minutes @ 1540.

Restarted @ ~ 5:55 & brought directly to 1640C.

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Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

644-26-88

IBM Technical Notebook

LEAK TESTING - SECTOR HIGH VAC

25 millitor after continued pumping through system  
STARTING WITH roughing valve

Will check pumpdown through HVAC valve alone  
tomorrow.

4/27 → vacation

4/28 Pump down through high vac initially unsuccessful, must  
have been stuck valve, but after freeing can get down  
to ~ 50 millitor in 15 minutes. Will continue pumping.

1/2 40

Down to 10 thru rough, 30 w/ HVAC only.

Rather quick leak-back when both closed off indicating  
leaks in system:

- 1) FURNACE
- 2) Elbow connection
- 3) Pump

See page 78

5/13 Promised CSS test Monday (Chad!)

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5/13

First Milling - AutoSeed - Teflon liner C3

48.17 g known, but "few" added before total processed wght. checked

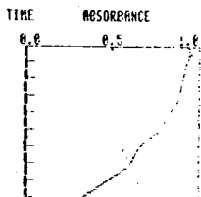
49.69 g yield

HORIBA CPRA-500  
 PARTICLE ANALYZER  
 DATE 5/13  
 SAMPLE C3-Box I  
 SOLVENT ISO  
 Teflon liner  
 CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CHE) 10.0 (PP)  
 D(MIN) 1.00 (PP)  
 D(DIV) 1.00 (PP)  
 SPEED 500 (RPM)

TIME 6 H 4 MIN 20 SEC

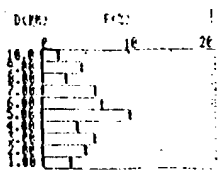
DATE



DISTRIBUTION TABLE (BY VOL.)

| D(CHE)    | F(2)      | R(2)  |
|-----------|-----------|-------|
| 10.0      | 49.7      | 49.7  |
| 10.0-9.0  | 1.0       | 51.6  |
| 9.00-8.00 | 4.5       | 56.1  |
| 8.00-7.00 | 2.7       | 58.8  |
| 7.00-6.00 | 6.1       | 64.9  |
| 6.00-5.00 | 6.9       | 71.7  |
| 5.00-4.00 | 10.2      | 81.9  |
| 4.00-3.00 | 4.0       | 85.9  |
| 3.00-2.00 | 6.0       | 91.9  |
| 2.00-1.00 | 5.0       | 96.8  |
| 1.00-0.00 | 3.2       | 100.0 |
| D(AVE)    | 9.85 (PP) |       |

DISTRIBUTION GRAPH (BY VOL.)



The above  
 and witnessed by

PASS II 5/16

47.6 g yield: much fluffier, looks  
 ~ like 3um powder.

IMMEDIATELY REMILLING

pg. 66 for PSD sheets ~2g loss!

PASS III 45.8  
 45.8

PASS IV 44.5  
 ~ 18.0 5 pellets  
 26.5

High large particle % 47.7 vs 18 for C2

overall ave. ~10 vs 5-6 for C2

however distribution seems similar { some  
 bypassing must have occurred.

Will work on Tuesday.

Date

and  
 by

Date

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Bi/Cu 25/75 erodable packed, sinter overnite in Ar/H<sub>2</sub>(5)  
 @ 750C.

#1 → < 100 mesh Cu, spherical (new)

#2 → <sup>10mm</sup> ~~100 mesh~~ ~~spherical Cu~~ (old)

#3 → penetration 10µm spherical

|      |             |     |             |
|------|-------------|-----|-------------|
| #2:  | 1.25/5.01   | #1: | 1.25/5.00   |
|      | 6.34        |     | 6.35        |
| ceux | <u>1.34</u> |     | <u>1.35</u> |
|      | 5.00        |     | 5.00        |

POST 6.31 6.32

8.0-8.5mm L 8.37

9.65-9.75mm dia 9.65-10.0

After interruptions: 5/24/ start cut { polishing  
 6/8/88 Finish: 6/8/88 after

{ Porosity is reduced, and 3<sup>rd</sup> 'oxide' has been eliminated }  
 (grey)  
 in forming gas.

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68 C3-P1-5 Green Data { IBM Technical Notebook } { Picked up mill test on }  
 150275 G mm mm { Material ruined }  
 C3P1 3.59 1.470 0.74 0.80 70.5  
3.33  
 C3P2 3.33 1.477 0.442 0.757 4.90 69%  
 2.93  
 C3P3 3.58 1.472 0.478 0.813 4.40 69%  
 C3P4 3.37 1.476 0.440  
 C3P5 3.53 1.474 0.471 5.52 87 even w/ cracking  
 3.19! 1.331 0.415 0.577 pack OK. I think.  
 Mill no good.

NOTES: PELLETS SEEM TO HAVE SHED ORGANIC/GAS?!  
 looks like the pellet milled in plastic container.  
 15026 UNL 6700 20% → 550, 10% → 975, 2 HRS

C3P6 2.52 1.50 0.32 4.46 70.1%  
 coarse 2.50 1.482 0.316 0.565 4.55 71%  
 0.55

The above understood  
 and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
 by \_\_\_\_\_

Date \_\_\_\_\_

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Calcinations - 750C IN @ 8:00 P.M. 5/17/88 out 9:00 5/18<sup>AM</sup> 69

TiO<sub>2</sub> - Genec 39g

$$\begin{array}{r} 16.3620 \\ - .8610 \\ \hline 15.501 \end{array} \text{ g TiO}_2 \text{ weighed}$$

5/18  
Post

$$\begin{array}{r} 105.0174 \\ 104.9395 \\ \hline 0.0779 \end{array} \text{ gaining } \Delta T > \Delta T_{\text{CO}_2}$$

$$15.501 = 0.5\% +$$

$$\begin{array}{r} 89.4610 \text{ crux } \Delta \\ 105.0174 \text{ crux + TiO}_2 \end{array}$$

$$\text{EQ} \rightarrow \begin{array}{r} 105.0084 \\ 105.0174 \\ \hline 0.0090 \end{array}$$

$$15.5564 \text{ g TiO}_2 \text{ by difference}$$

$$99.64\% \rightarrow 0.3\% \Delta + 0.0554$$

$$0.0090 / 0.0779 = 88.5\% \text{ back}$$

SrCO<sub>3</sub>

$$\begin{array}{r} 18.4193 \\ 0.8720 \\ \hline 17.5473 \end{array} \rightarrow \begin{array}{r} 0.8732 \\ 17.5441 \end{array}$$

$$\Delta 0.0032 \approx \Delta \Delta \text{Dis} !!$$

$$\begin{array}{r} 109.9615 \\ 92.3660 \\ \hline 17.5955 \end{array} \Delta + 0.0514$$

$$\Delta \Delta \text{Dis} \Rightarrow 0.004 \text{ g} \sim \text{4mg calibration}$$

$$\text{Post } \begin{array}{r} 109.9615 \\ 109.8870 \\ \hline 0.0745 \end{array} \text{ gaining } 17.5441 = 0.4\%$$

$$\text{EQ } \begin{array}{r} 109.9510 \\ 109.9615 \\ \hline 0.0105 \end{array} 85.6\% \text{ back}$$

5/19 TiO<sub>2</sub> { ~~SrCO<sub>3</sub>~~ 2<sup>nd</sup> Cal POST

SrCO<sub>3</sub>

$$\begin{array}{r} 105.0174 \\ 104.8670 \\ \hline .15 \end{array} (-0.0003 \text{ cal})$$

$$\sim 1\%$$

$$\begin{array}{r} 109.9615 \\ 109.8580 \\ \hline 0.1035 \end{array} (-0.0003 \text{ cal})$$

$$\sim 0.6\%$$

The above understood and witnessed by

Date

and by

Date



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70

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IBM Technical Notebook

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HF Silicon Etch/Wash/Buffer Solns.

~~80g~~ { 80g  $\text{NH}_4\text{F}$  in 120g  $\text{H}_2\text{O}$  (distilled)  $\rightarrow$  ~120cc 40 wt. %  $\text{NH}_4\text{F}$  REAGENT  
actual soln is 40:1 ~~10:1~~  $\sim 170\text{cc}$

BHF  $\rightarrow$  40 parts  $\text{NH}_4\text{F}$  reagent : 1 part HF (49 wt %) soln.

QUENCH  $\rightarrow$  10:1 DI :  $\text{NH}_4\text{OH}$  reagent 50ml:500ml

BHF clean  $\rightarrow$  10:1:2.2 ( $\text{NH}_4\text{F}$ :HF:Glycerin)  
reagent 49

16(10)=160 16(1)=16 16(2.2)=35.2 = 211 ml  
320  
350  
(190) (35) (77)

MSG:FROM: SARDESAI--FSHVMCC TO: MDT --YKIVMT  
To: MDT --YKIVMT

05/18/88 12:39:40

From: Viraj Sardesai  
8-533-8545, SCL Pers Metals, GTD E. Fishkill  
IBM INTERNAL USE ONLY (Unless otherwise specified)  
SUBJECT: BHF concentrations used in SCL

Michael,

We use 40:1 BHF for pre platinum, emitter screen ox removal and for s metal preclean.

The chemical is commercially available premixed solution and has 40 parts (by volume) of 40 wt pct  $\text{NH}_4\text{F}$  solution mixed with 1 part of 49 wt pct HF solution. Both  $\text{NH}_4\text{F}$  and HF are in aqueous solutions. Manufacturer specs the HF concentration to 0.61 to 0.77 moles per liter and specific gravity of 1.106.

For S postL/O BHF clean 10:1:2.2 ( $\text{NH}_4\text{F}$ :HF:Glycerin) is used prepared similarly and quenched in 10:1  $\text{NH}_4\text{OH}$  solution (28 Wt pct  $\text{NH}_4\text{OH}$  solution diluted 10 times its volume in DI water).

cc: SZEC SY --FSHVMCC

HOUGHTON--FSHVMCC

Regards,

VIRAJ

FSHVMCC(SARDESAI),D/11G B/322 Z/5T1

\*\*\*\*\* OUR TEAMWORK MAKES THE DIFFERENCE ! \*\*\*\*\*

BHF concentrations used in SCL

BHF

BHF CLEAN

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IBM Technical Notebook - mill #2

73

5/18 Polymilling

| PS  | 40g batch | YIELD | PSD1          | 2    | A                                   |
|-----|-----------|-------|---------------|------|-------------------------------------|
| I   |           | 36.8  | 6.94          | 4.84 | 3                                   |
| II  |           | 33.4  | 3.65          | 3.21 | 3                                   |
| III |           | 31.3  | 3.53          |      | (2) bag charger required            |
| IV  |           | 28.4  | <u>2.98</u> ! |      | 3 actually higher erroneous 7% @ 10 |
| V   |           | 25.75 | <u>3.1</u> !  |      | 2.5 new bag                         |

200

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by \_\_\_\_\_

Date \_\_\_\_\_

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 anything possibly new and inventive.

ISO 28,

74

IBM Technical Notebook

MARGINAL GREGG  
 DENSITIES

|      |      |       |       |        |      |               |
|------|------|-------|-------|--------|------|---------------|
| C3P6 | 3.29 | 1.474 | 0.471 |        | 4.11 | 64.6          |
|      | 3.23 | 1.343 | 0.416 | 0.80   | 5.48 | <u>86.2</u> ! |
|      |      |       |       | 0.59   |      |               |
| C3P7 | 3.19 | 1.476 | 0.455 |        | 4.10 | 64.5          |
|      | 3.13 | 1.343 | 0.404 | 0.779  | 5.49 | 86.3          |
|      |      |       |       | 0.57   |      |               |
| C3P8 | 3.21 | 1.473 | 0.462 | 0.787  |      | 64.1          |
|      | 3.16 | 1.341 | 0.409 | 0.577  | 5.48 | 86.2          |
|      |      |       |       |        |      | } TO KING-TU  |
| C3P9 | 3.08 | 1.474 | 0.441 |        | 4.09 | 64.3          |
|      | 3.02 | 1.336 | 0.391 | 0.7525 | 5.51 | <u>86.6</u>   |
|      |      |       |       | 0.548  |      |               |

NOTES: PELLETS W @ 4:55 with flowing O<sub>2</sub> (bottled, dessicated)  
 Heating started @ 5:15 @ 20°/min (97C @ start)  
 @ 265C cut back to 10°/min; to reach sinter T' @ 6:35 p.m.  
 Sintering @ 975C for 2HRS. till 8:35 p.m.  
 Quench ! remove.

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# IBM Technical Notebook

75

995C sinter  
CSP10 3.18 1.474 0.453 4.114 64.7  
3.11 1.338 0.399 0.773cc 5.54 87.2  
0.561

no (appreciable) liq.  $\phi$ !

T3 "dry"  
yield Pass  $\Delta$  MILL#1  
10.35  $\phi$

Ave. part dia.  
<100 mesh

29.~ I 10 ! 12g leaks 3.29

21.5 II 8 ! ~1g leak 3.11

18.5 III 3 ! 4.0<sup>+</sup> g of ~2.0 $\mu$ m powder in mill neck

22.4 total max yield

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by \_\_\_\_\_

Date \_\_\_\_\_

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"T3" pellets

IBM Technical Notebook

77

C3P10-18  
9750

|         |      |       |       |       |       |             |
|---------|------|-------|-------|-------|-------|-------------|
| C3P10 ① | 3.14 | 1.461 | 0.473 |       | 3.975 | 62.50       |
| ✓ 3.08  |      | 1.308 | 0.400 | 0.79  | 5.75  | <u>90.4</u> |
|         |      |       |       | 0.536 |       |             |

|         |        |       |       |      |      |             |
|---------|--------|-------|-------|------|------|-------------|
| C3P12 ② | 3.28   | 1.462 | 0.495 |      |      |             |
| C       | ✓ 3.21 | 1.308 | 0.417 | 0.56 | 5.73 | <u>90.0</u> |

|         |      |                  |       |                  |       |                  |
|---------|------|------------------|-------|------------------|-------|------------------|
| C3P12 ③ | 3.04 | 1.463            | 0.450 |                  |       |                  |
|         | 2.97 | <del>1.307</del> | 0.388 | <del>0.552</del> | 5.68  | <del>89.31</del> |
|         |      | <del>1.310</del> | 0.385 | 0.523            | 5.756 | 90.5             |
|         |      | 1.306            |       | 0.516            |       |                  |

RECHECK TOMORROW

|        |      |       |       |       |        |               |
|--------|------|-------|-------|-------|--------|---------------|
| C3P14  | 3.21 | 1.464 | 0.473 |       |        |               |
| ✓ 3.14 |      | 1.308 | 0.405 | 0.548 | 5.77-8 | <u>90.7-9</u> |
|        |      | 1.306 |       |       |        |               |

10000

|       |      |       |       |       |      |       |
|-------|------|-------|-------|-------|------|-------|
| C3P15 | 3.04 | 1.461 | 0.458 |       |      |       |
|       | 2.97 | 1.298 | 0.386 |       | 5.81 | 91.35 |
|       |      |       |       | 0.511 |      |       |

|                |      |       |       |       |      |      |
|----------------|------|-------|-------|-------|------|------|
| C3P16 (pulsed) | 3.08 | 1.466 | 0.457 |       |      |      |
|                | 3.02 | 1.301 | 0.390 | 0.519 | 5.82 | 91.5 |

|       |        |       |       |       |      |             |
|-------|--------|-------|-------|-------|------|-------------|
| C3P17 | 3.28   | 1.464 | 0.492 |       | 5.75 | <u>90.4</u> |
|       | 3.22   | 1.298 | 0.422 | 0.568 | 5.82 | 91.5        |
|       | (3.28) |       |       |       |      | chip offed  |

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and by

Date



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78 6/7/88

IBM Technical Notebook

Centorr HVAC system close to finished with leak testing,  
preliminary operation checks.

System mechanical pump down < 20-30 minutes

Turbomolecular ↓ down → to  $5 \times 10^{-5}$  within 1 hr  
with attainment of mid  $6^{-5}$  by 1:00 p.m.  
Start was 9:15 originally.

Block-off flange, new Centorr purge / plug fittings still  
needed. Failure leak test reg.

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

Bi/Cu Free-Crucible Sinter Vacuum Run

To glass shop 6/7/88. Batch size to be 4.0 g to allow for ease of manipulation during sealing of quartz tube.

$$4.0 (0.25) = 1.00 \text{ g Bi}$$

$$\downarrow (0.75) = 3.00 \text{ g Cu (will use 10 } \mu\text{m Cu powder)}$$

$$\begin{array}{r} \text{Bi} \rightarrow 1.00 (0.99) \\ \text{Cu to } 4.03 \\ \text{Cu } 3.03 \end{array}$$

$$\text{from JAR } 4.02 (1)$$

$$\begin{array}{r} \text{cruc } 1.33 \\ \text{w/ mix } 5.33 (4) \\ 4.00 (1) \\ \hline 4.04 \end{array}$$

$$\begin{array}{r} \sim 24.8\% \quad \sim 25 \\ 75.2\% \quad 75 \end{array}$$

Ped - spilled in glass shop

6/9 New crucible shape/size for stability

Let's take 5.0 g batch

$$1.25/5.0 (\pm 0.01)$$

$$\begin{array}{r} \text{crucible } 3.35 \\ \text{w/ mix } 8.35 \\ \hline 5.00 \end{array}$$

6/14 After overnite sinter & removal from quartz tube

cruc. & sinter 8.30 g (some spillage in tube before heat treatment)

no appreciable vapor product seen

CONCLUSIONS: Vacuum doesn't appear to work as well as Ar/H<sub>2</sub>. Sample full of holes, but no evidence of oxidation, so holes are real. Again, no evidence of vapor phase deposition in tube.

IBM Technical Notebook

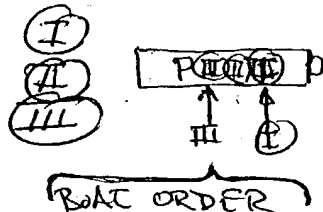
80 6/14/88

To do: 10, 20, 25 % in Ar/H<sub>2</sub>(g)

~~MONDAY~~ (VACATION)  
RUN!

WENDS 6/22/88

5 gram batches: 0.25 (5) = 1.25 B. / 3.75 C  
 0.20 (5) = 1.00 B. / 4.00 C  
 0.10 (5) = .5 B. / 4.5 C



(I) 5 gram w/ new conical crucible  
 mix 9.03  
 tare 4.03  
 5.00  
 ↑  
 PRE

voids, but some areas seem OK.  
 less small voids, some good regions versus (II),  
 however large voids a mystery. Need  
 repeating, maybe longer times.

(II) 9.00  
 tare 4.00  
 5.00

seems very good, no large voids, mix exam next  
 microscopic exam should show many small "pockets"  
 or voids. Usually circular.

(III) 6.31  
 tare 1.31  
 5.00 'normal loss possible'

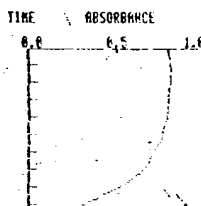
did not densify fully

## Administrative Notes

Srtio<sub>2</sub> Milling ResultsMORIPA CAPA-SEE  
PARTICLE ANALYZERDATE 3/24/88  
SAMPLE Srtio<sub>2</sub>-B  
SOLVENT ISO  
MTI-MED\* CONDITIONS  
SLIGHT IMPROVEMENTSOLV. VISC 2.10(CP)  
SOLV. DENS 6.79(G/CC)  
SAMP. DENS 4.81(G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00(PM)  
D(DIV) 1.00(PM)  
SPEED 500. (RPM)

\* TIME 0 H 6 MIN 0 SEC

\* DATA D=0.8

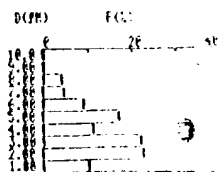


## \* DISTRIBUTION TABLE (BY VOL.)

| D(PH)       | F(%) | R(%)  |
|-------------|------|-------|
| 10.0 -      | 0.0  | 0.0   |
| 10.0 - 9.0  | 0.0  | 0.0   |
| 9.00 - 8.00 | 0.0  | 0.0   |
| 8.00 - 7.00 | 2.9  | 2.9   |
| 7.00 - 6.00 | 4.4  | 8.4   |
| 6.00 - 5.00 | 0.5  | 17.2  |
| 5.00 - 4.00 | 17.1 | 34.2  |
| 4.00 - 3.00 | 11.1 | 45.4  |
| 3.00 - 2.00 | 22.8 | 67.4  |
| 2.00 - 1.00 | 22.5 | 89.9  |
| 1.00 - 0.00 | 10.2 | 100.0 |

D(AVE) 2.79 (PM)

## \* DISTRIBUTION GRAPH (BY VOL.)

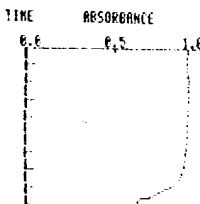
MORIPA CAPA-SEE  
PARTICLE ANALYZERDATE 3/21/88  
SAMPLE Srtio<sub>2</sub>-DRC2  
SOLVENT ISO  
MTI-S

## \* CONDITIONS

SOLV. VISC 2.10(CP)  
SOLV. DENS 6.79(G/CC)  
SAMP. DENS 4.81(G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00(PM)  
D(DIV) 1.00(PM)  
SPEED 500. (RPM)

\* TIME 0 H 6 MIN 0 SEC

\* DATA

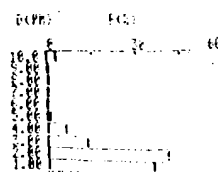


## \* DISTRIBUTION TABLE (BY VOL.)

| D(PH)       | F(%) | R(%)  |
|-------------|------|-------|
| 10.0 -      | 0.0  | 0.0   |
| 10.0 - 9.0  | 2.9  | 2.9   |
| 9.00 - 8.00 | 0.0  | 2.9   |
| 8.00 - 7.00 | 0.0  | 2.9   |
| 7.00 - 6.00 | 0.0  | 2.9   |
| 6.00 - 5.00 | 0.0  | 2.9   |
| 5.00 - 4.00 | 0.0  | 3.0   |
| 4.00 - 3.00 | 5.9  | 9.0   |
| 3.00 - 2.00 | 13.4 | 23.0  |
| 2.00 - 1.00 | 41.0 | 64.0  |
| 1.00 - 0.00 | 35.5 | 100.0 |

D(AVE) 1.34 (PM)

## \* DISTRIBUTION GRAPH (BY VOL.)

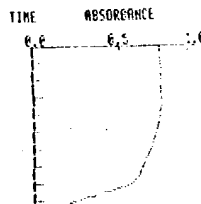
MORIPA CAPA-SEE  
PARTICLE ANALYZERDATE 3/24/88  
SAMPLE Srtio<sub>2</sub>-DRC2  
SOLVENT ISO  
MTI

## \* CONDITIONS

SOLV. VISC 2.10(CP)  
SOLV. DENS 6.79(G/CC)  
SAMP. DENS 4.81(G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00(PM)  
D(DIV) 1.00(PM)  
SPEED 500. (RPM)

\* TIME 0 H 6 MIN 0 SEC

\* DATA

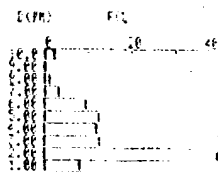


## \* DISTRIBUTION TABLE (BY VOL.)

| D(PH)       | F(%) | R(%)  |
|-------------|------|-------|
| 10.0 -      | 0.0  | 0.0   |
| 10.0 - 9.0  | 1.0  | 1.0   |
| 9.00 - 8.00 | 0.0  | 1.0   |
| 8.00 - 7.00 | 1.6  | 2.6   |
| 7.00 - 6.00 | 2.9  | 5.5   |
| 6.00 - 5.00 | 9.5  | 15.0  |
| 5.00 - 4.00 | 12.5 | 27.5  |
| 4.00 - 3.00 | 12.1 | 39.6  |
| 3.00 - 2.00 | 12.6 | 52.2  |
| 2.00 - 1.00 | 39.6 | 91.8  |
| 1.00 - 0.00 | 7.9  | 100.0 |

D(AVE) 2.20 (PM)

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Administrative Notes

C3 MILLING RESULTS - T1: Teflon T2: Poly T3: PolyO

T1

MORIBA CAPP-500  
PARTICLE ANALYZER

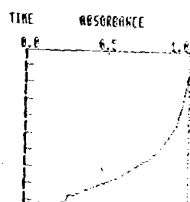
DATE 5/17  
SAMPLE C3-P1  
SOLVENT ISO

\* CONDITIONS

T1 →  
SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CMAX) 10.0 (PM)  
D(CMIN) 1.00 (PM)  
D(CDIV) 1.00 (PM)  
SPEED 500 (RPM)

\* TIME 0 H 4 MIN 20 SEC

\* DATA

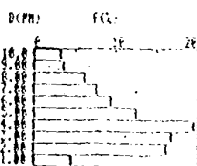


\* DISTRIBUTION TABLE (BY VOL.)

| D(CPM)   | F(C) | R(C)  |
|----------|------|-------|
| 10.0-9.0 | 0.0  | 0.0   |
| 9.0-8.0  | 2.0  | 3.2   |
| 8.0-7.0  | 3.6  | 6.5   |
| 7.0-6.0  | 6.1  | 13.0  |
| 6.0-5.0  | 7.7  | 20.7  |
| 5.0-4.0  | 9.5  | 30.2  |
| 4.0-3.0  | 12.6 | 42.0  |
| 3.0-2.0  | 15.6 | 62.4  |
| 2.0-1.0  | 16.8 | 75.2  |
| 1.0-0.0  | 16.2 | 95.4  |
| 0.0-0.0  | 4.6  | 100.0 |

D(AVE) 3.63 (PM)

\* DISTRIBUTION GRAPH (BY VOL.)



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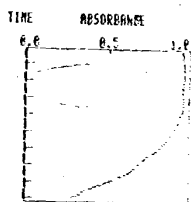
DATE 5/17  
SAMPLE C3-P1  
SOLVENT IS

\* CONDITIONS

D~0.97  
SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CMAX) 10.0 (PM)  
D(CMIN) 1.00 (PM)  
D(CDIV) 1.00 (PM)  
SPEED 500 (RPM)

\* TIME 0 H 4 MIN 20 SEC

\* DATA

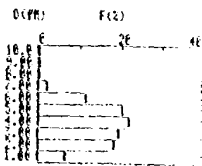


\* DISTRIBUTION TABLE (BY VOL.)

| D(CPM)   | F(C) | R(C)  |
|----------|------|-------|
| 10.0-9.0 | 0.0  | 0.0   |
| 9.0-8.0  | 0.0  | 0.0   |
| 8.0-7.0  | 0.0  | 0.0   |
| 7.0-6.0  | 0.0  | 0.0   |
| 6.0-5.0  | 11.5 | 13.0  |
| 5.0-4.0  | 26.2 | 33.0  |
| 4.0-3.0  | 21.5 | 50.7  |
| 3.0-2.0  | 19.4 | 75.1  |
| 2.0-1.0  | 16.3 | 93.4  |
| 1.0-0.0  | 6.6  | 100.0 |

D(AVE) 3.26 (PM)

\* DISTRIBUTION GRAPH (BY VOL.)



MORIBA CAPP-500  
PARTICLE ANALYZER

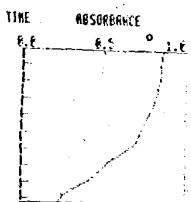
DATE 5/17  
SAMPLE C3-P1  
SOLVENT ISO

\* CONDITIONS

D~0.9  
SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CMAX) 10.0 (PM)  
D(CMIN) 1.00 (PM)  
D(CDIV) 1.00 (PM)  
SPEED 500 (RPM)

\* TIME 0 H 4 MIN 20 SEC

\* DATA

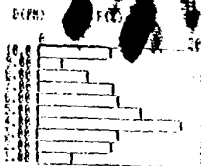


\* DISTRIBUTION TABLE (BY VOL.)

| D(CPM)   | F(C) | R(C)  |
|----------|------|-------|
| 10.0-9.0 | 0.0  | 0.0   |
| 9.0-8.0  | 0.0  | 0.0   |
| 8.0-7.0  | 0.0  | 0.0   |
| 7.0-6.0  | 0.0  | 0.0   |
| 6.0-5.0  | 9.0  | 9.0   |
| 5.0-4.0  | 0.9  | 10.0  |
| 4.0-3.0  | 2.0  | 21.0  |
| 3.0-2.0  | 6.0  | 27.7  |
| 2.0-1.0  | 9.2  | 36.0  |
| 1.0-0.0  | 9.0  | 46.0  |
| 0.0-0.0  | 12.6 | 59.2  |
| 0.0-0.0  | 17.6 | 76.9  |
| 0.0-0.0  | 9.0  | 86.7  |
| 0.0-0.0  | 9.0  | 95.0  |
| 0.0-0.0  | 4.2  | 100.0 |

D(AVE) 4.73 (PM)

\* DISTRIBUTION GRAPH (BY VOL.)



# Administrative Notes

T2 Part I

## NORIB CAPH-SEE PARTICLE ANALYZER

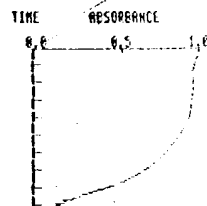
DATE 5/19  
SAMPLE C3-PI-T2  
SOLVENT ISO

### • CONDITIONS

SOLV. VISC 2.18 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 0.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (PPM)

• TIME 0 H 4 MIN 26 SEC

• DATA ~0.9

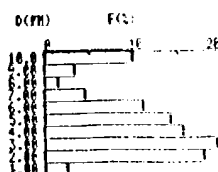


### • DISTRIBUTION TABLE (BY VOL.)

| D(PH)      | F(2) | F(2)  |
|------------|------|-------|
| 10.0 - 9.0 | 0.0  | 0.0   |
| 9.0 - 8.0  | 0.0  | 0.0   |
| 8.0 - 7.0  | 1.5  | 13.2  |
| 7.0 - 6.0  | 4.5  | 15.2  |
| 6.0 - 5.0  | 11.2 | 30.4  |
| 5.0 - 4.0  | 14.1 | 44.5  |
| 4.0 - 3.0  | 15.6 | 60.1  |
| 3.0 - 2.0  | 19.4 | 79.5  |
| 2.0 - 1.0  | 18.8 | 97.5  |
| 1.0 - 0.0  | 2.5  | 100.0 |

D(AVE) 3.65 (PM)

### • DISTRIBUTION GRAPH (BY VOL.)



## NORIB CAPH-SEE PARTICLE ANALYZER

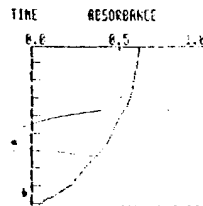
DATE 5/19  
SAMPLE C3-PI-T2  
SOLVENT ISO

### • CONDITIONS

SOLV. VISC 2.18 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 0.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (PPM)

• TIME 0 H 4 MIN 28 SEC

• DATA ~0.57

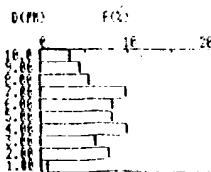


### • DISTRIBUTION TABLE (BY VOL.)

| D(PH)      | F(2) | F(2)  |
|------------|------|-------|
| 10.0 - 9.0 | 36.4 | 36.4  |
| 9.0 - 8.0  | 3.2  | 35.6  |
| 8.0 - 7.0  | 4.2  | 43.5  |
| 7.0 - 6.0  | 5.5  | 45.4  |
| 6.0 - 5.0  | 5.8  | 59.2  |
| 5.0 - 4.0  | 8.2  | 67.5  |
| 4.0 - 3.0  | 8.1  | 75.6  |
| 3.0 - 2.0  | 9.5  | 85.4  |
| 2.0 - 1.0  | 6.2  | 91.6  |
| 1.0 - 0.0  | 7.8  | 99.2  |
| 0.0 - 0.0  | 0.7  | 100.0 |

D(AVE) 6.94 (PM)

### • DISTRIBUTION GRAPH (BY VOL.)



## NORIB CAPH-SEE PARTICLE ANALYZER

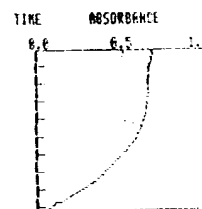
DATE 5/19  
SAMPLE C3-PI-T2  
SOLVENT ISO

### • CONDITIONS

SOLV. VISC 2.18 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 0.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (PPM)

• TIME 0 H 4 MIN 26 SEC

• DATA ~0.67

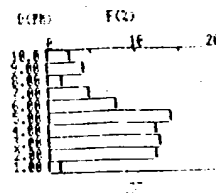


### • DISTRIBUTION TABLE (BY VOL.)

| D(PH)      | F(2) | F(2)  |
|------------|------|-------|
| 10.0 - 9.0 | 27.1 | 27.1  |
| 9.0 - 8.0  | 2.5  | 29.6  |
| 8.0 - 7.0  | 4.1  | 33.7  |
| 7.0 - 6.0  | 1.5  | 35.2  |
| 6.0 - 5.0  | 4.6  | 39.9  |
| 5.0 - 4.0  | 7.9  | 47.8  |
| 4.0 - 3.0  | 13.8 | 61.6  |
| 3.0 - 2.0  | 12.3 | 73.9  |
| 2.0 - 1.0  | 12.7 | 86.6  |
| 1.0 - 0.0  | 12.2 | 98.8  |
| 0.0 - 0.0  | 1.2  | 100.0 |

D(AVE) 4.84 (PM)

### • DISTRIBUTION GRAPH (BY VOL.)



# Administrative Notes

T2 PART 2

MORIBA CAPA-506  
PARTICLE ANALYZER

DATE 5/19  
SAMPLE CS-P2-T2  
SOLVENT 150

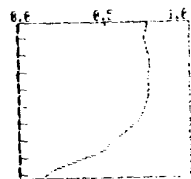
## • CONDITIONS

SOLV. VISC 2.18(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 6.36(G/CC)  
D(MAX) 10.0 (PH)  
D(MIN) 1.00(PH)  
D(DIV) 1.00(PH)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA ~0.7

TIME ABSORBANCE



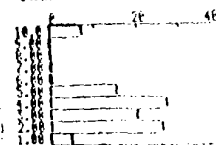
## • DISTRIBUTION TABLE (BY VOL.)

| D(PH)      | F(2) | R(2)  |
|------------|------|-------|
| 10.0 - 9.0 | 0.0  | 0.0   |
| 9.0 - 8.0  | 7.2  | 7.2   |
| 8.0 - 7.0  | 0.0  | 7.2   |
| 7.0 - 6.0  | 0.0  | 7.2   |
| 6.0 - 5.0  | 0.3  | 7.6   |
| 5.0 - 4.0  | 15.1 | 22.7  |
| 4.0 - 3.0  | 27.0 | 49.7  |
| 3.0 - 2.0  | 20.0 | 69.7  |
| 2.0 - 1.0  | 25.0 | 95.3  |
| 1.0 - 0.0  | 4.7  | 100.0 |

D(AVE) 2.50 (PH)

## • DISTRIBUTION GRAPH (BY VOL.)

D(PH) F(2)



MORIBA CAPA-506  
PARTICLE ANALYZER

DATE 5/19  
SAMPLE CS-P2-T2  
SOLVENT 150

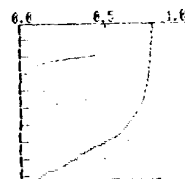
## • CONDITIONS

SOLV. VISC 2.18(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 6.36(G/CC)  
D(MAX) 10.0 (PH)  
D(MIN) 1.00(PH)  
D(DIV) 1.00(PH)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA ~0.7

TIME ABSORBANCE



## • DISTRIBUTION TABLE (BY VOL.)

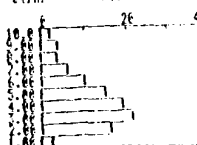
| D(PH)      | F(2) | R(2)  |
|------------|------|-------|
| 10.0 - 9.0 | 0.0  | 0.0   |
| 9.0 - 8.0  | 2.1  | 2.1   |
| 8.0 - 7.0  | 3.9  | 6.0   |
| 7.0 - 6.0  | 3.7  | 9.8   |
| 6.0 - 5.0  | 6.2  | 16.0  |
| 5.0 - 4.0  | 10.1 | 26.0  |
| 4.0 - 3.0  | 15.0 | 41.0  |
| 3.0 - 2.0  | 19.0 | 60.0  |
| 2.0 - 1.0  | 21.4 | 81.5  |
| 1.0 - 0.0  | 16.0 | 97.5  |
| 0.0 - 0.0  | 2.5  | 100.0 |

D(AVE) 3.53 (PH)

NO MILLING / BAG CHANGE

## • DISTRIBUTION GRAPH (BY VOL.)

D(PH) F(2)



MORIBA CAPA-506  
PARTICLE ANALYZER

DATE 5/19/88  
SAMPLE CS-P2-T2  
SOLVENT 150

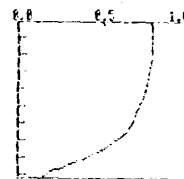
## • CONDITIONS

SOLV. VISC 2.18(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 6.36(G/CC)  
D(MAX) 10.0 (PH)  
D(MIN) 1.00(PH)  
D(DIV) 1.00(PH)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

TIME ABSORBANCE



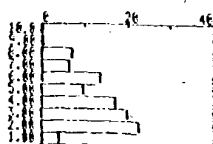
## • DISTRIBUTION TABLE (BY VOL.)

| D(PH)      | F(2) | R(2)  |
|------------|------|-------|
| 10.0 - 9.0 | 0.0  | 0.0   |
| 9.0 - 8.0  | 0.0  | 0.0   |
| 8.0 - 7.0  | 0.0  | 0.0   |
| 7.0 - 6.0  | 7.0  | 7.0   |
| 6.0 - 5.0  | 6.4  | 13.4  |
| 5.0 - 4.0  | 13.4 | 26.8  |
| 4.0 - 3.0  | 9.0  | 36.0  |
| 3.0 - 2.0  | 17.1 | 53.0  |
| 2.0 - 1.0  | 26.0 | 79.0  |
| 1.0 - 0.0  | 22.4 | 96.0  |
| 0.0 - 0.0  | 4.0  | 100.0 |

D(AVE) 3.21 (PH)

## • DISTRIBUTION GRAPH (BY VOL.)

D(PH) F(2)



# Administrative Notes

T2 (cond.)

NORIDA CAPA-500  
PARTICLE ANALYZER

DATE

SAMPLE C3-P5-T2

SOLVENT

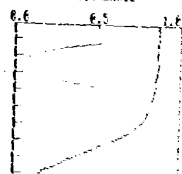
## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (RPM)

• TIME 6 H 4 MIN 20 SEC

• DATA 0.87

TIME ABSORBANCE

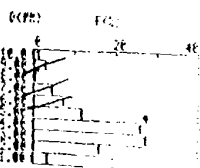


## • DISTRIBUTION TABLE (BY VOL.)

| D(PH)    | F(2)  | R(2)  |
|----------|-------|-------|
| 10.0-9.0 | 0.0   | 0.0   |
| 9.0-8.0  | 1.2   | 1.2   |
| 8.0-7.0  | 2.4   | 3.6   |
| 7.0-6.0  | 4.8   | 7.2   |
| 6.0-5.0  | 7.2   | 12.0  |
| 5.0-4.0  | 14.4  | 21.6  |
| 4.0-3.0  | 28.8  | 43.2  |
| 3.0-2.0  | 57.6  | 86.4  |
| 2.0-1.0  | 115.2 | 172.8 |
| 1.0-0.0  | 230.4 | 345.6 |

D(AVE) 3.16 (PM)

## • DISTRIBUTION GRAPH (BY VOL.)



NORIDA CAPA-500  
PARTICLE ANALYZER

DATE

SAMPLE C3-P5-T2

SOLVENT

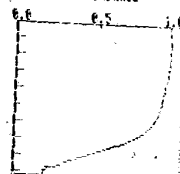
## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (RPM)

• TIME 6 H 4 MIN 20 SEC

• DATA ~0.9

TIME ABSORBANCE

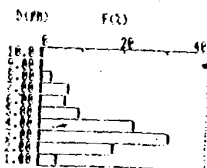


## • DISTRIBUTION TABLE (BY VOL.)

| D(PH)    | F(2)  | R(2)  |
|----------|-------|-------|
| 10.0-9.0 | 0.0   | 0.0   |
| 9.0-8.0  | 0.0   | 0.0   |
| 8.0-7.0  | 2.3   | 2.3   |
| 7.0-6.0  | 6.0   | 9.1   |
| 6.0-5.0  | 6.0   | 15.1  |
| 5.0-4.0  | 9.6   | 24.6  |
| 4.0-3.0  | 22.5  | 47.1  |
| 3.0-2.0  | 36.1  | 77.8  |
| 2.0-1.0  | 60.0  | 95.7  |
| 1.0-0.0  | 115.2 | 172.8 |

D(AVE) 2.91 (PM)

## • DISTRIBUTION GRAPH (BY VOL.)





# Administrative Notes

T1 versus T2 versus T3 for various passes

NORIE CIPA-500  
PARTICLE ANALYZER

DATE 6/23  
SAMPLE C3-PS-B  
SOLVENT 150

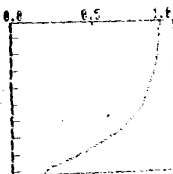
• CONDITION T3

SOLV. VISC 2.18(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 6.36(G/CC)  
D(CAN) 10.0 (PP)  
D(MIN) 1.00(PP)  
D(DIV) 1.00(PP)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA 0.9

TIME ABSORBANCE

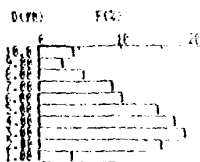


• DISTRIBUTION TABLE (BY VOL.)

| D(PH)     | F(C) | R(C)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 4.3  | 4.2   |
| 9.00-8.00 | 2.9  | 7.2   |
| 8.00-7.00 | 5.5  | 12.7  |
| 7.00-6.00 | 9.0  | 21.7  |
| 6.00-5.00 | 10.2 | 31.9  |
| 5.00-4.00 | 14.6 | 46.5  |
| 4.00-3.00 | 16.6 | 63.1  |
| 3.00-2.00 | 17.9 | 81.0  |
| 2.00-1.00 | 15.0 | 96.8  |
| 1.00-0.00 | 4.0  | 100.0 |

D(AVE) 3.70 (PP)

• DISTRIBUTION GRAPH (BY VOL.)



NORIE CIPA-500  
PARTICLE ANALYZER

DATE 5/12  
SAMPLE C3-PS  
SOLVENT

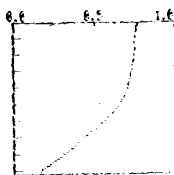
• CONDITIONS 0.5

SOLV. VISC 2.18(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 6.36(G/CC)  
D(CAN) 10.0 (PP)  
D(MIN) 1.00(PP)  
D(DIV) 1.00(PP)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA T1

TIME ABSORBANCE

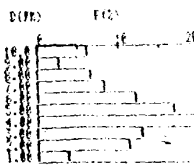


• DISTRIBUTION TABLE (BY VOL.)

| D(PH)     | F(C) | R(C)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 6.2  | 6.2   |
| 9.00-8.00 | 2.7  | 6.0   |
| 8.00-7.00 | 6.6  | 15.4  |
| 7.00-6.00 | 8.2  | 23.6  |
| 6.00-5.00 | 12.6 | 35.8  |
| 5.00-4.00 | 16.0 | 52.4  |
| 4.00-3.00 | 19.0 | 72.1  |
| 3.00-2.00 | 12.8 | 85.0  |
| 2.00-1.00 | 11.2 | 96.2  |
| 1.00-0.00 | 3.7  | 100.0 |

D(AVE) 4.14 (PP)

• DISTRIBUTION GRAPH (BY VOL.)



NORIE CIPA-500  
PARTICLE ANALYZER

DATE 12-11  
SAMPLE C3-PS  
SOLVENT

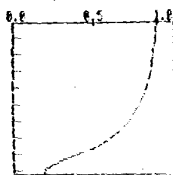
• CONDITIONS NO CHANGE  
MICROFILM REQUIRED

SOLV. VISC 2.18(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 6.36(G/CC)  
D(CAN) 10.0 (PP)  
D(MIN) 1.00(PP)  
D(DIV) 1.00(PP)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA T2

TIME ABSORBANCE

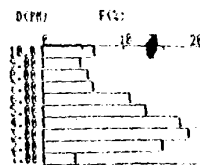


• DISTRIBUTION TABLE (BY VOL.)

| D(PH)     | F(C) | R(C)  |
|-----------|------|-------|
| 10.0      | 0.0  | 0.0   |
| 10.0-9.0  | 6.5  | 6.5   |
| 9.00-8.00 | 4.7  | 11.2  |
| 8.00-7.00 | 5.6  | 16.8  |
| 7.00-6.00 | 6.3  | 23.1  |
| 6.00-5.00 | 10.7 | 33.7  |
| 5.00-4.00 | 12.7 | 46.4  |
| 4.00-3.00 | 16.5 | 63.4  |
| 3.00-2.00 | 18.0 | 81.4  |
| 2.00-1.00 | 14.7 | 96.1  |
| 1.00-0.00 | 3.9  | 100.0 |

D(AVE) 3.70 (PP)

• DISTRIBUTION GRAPH (BY VOL.)



Administrative Notes

FINAL C3-T3- RESULTS: NECK, MIX & premix medium

HORIBA  
PARTICLE

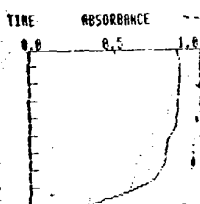
SAMPLE  
SOLVENT

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 8 H 4 MIN 20 SEC

• DATA

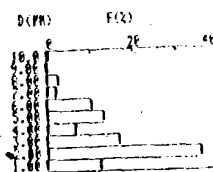


• DISTRIBUTION TABLE (BY VOL.)

| D (PM)    | F (Z) | R (Z) |
|-----------|-------|-------|
| 10.0      | 0.0   | 0.0   |
| 10.0-9.0  | 0.0   | 0.0   |
| 9.00-8.00 | 0.0   | 0.0   |
| 8.00-7.00 | 2.4   | 2.4   |
| 7.00-6.00 | 1.1   | 4.4   |
| 6.00-5.00 | 10.5  | 14.9  |
| 5.00-4.00 | 13.1  | 28.6  |
| 4.00-3.00 | 6.5   | 34.5  |
| 3.00-2.00 | 17.6  | 51.5  |
| 2.00-1.00 | 0     | 67.4  |
| 1.00-0.00 | 0     | 100.0 |

D(AVE) 2.00 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



HORIBA CAPA-500  
PARTICLE ANALYZER

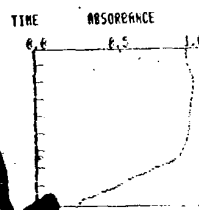
DATE 5/23  
SAMPLE C3-T3-MIX  
SOLVENT F32

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 8 H 4 MIN 20 SEC

• DATA D=0.9

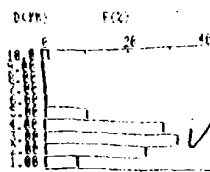


• DISTRIBUTION TABLE (BY VOL.)

| D (PM)    | F (Z) | R (Z) |
|-----------|-------|-------|
| 10.0      | 0.0   | 0.0   |
| 10.0-9.0  | 0.0   | 0.0   |
| 9.00-8.00 | 0.0   | 0.0   |
| 8.00-7.00 | 0.0   | 0.0   |
| 7.00-6.00 | 0.0   | 0.0   |
| 6.00-5.00 | 0.0   | 0.0   |
| 5.00-4.00 | 0.0   | 0.0   |
| 4.00-3.00 | 27.7  | 38.6  |
| 3.00-2.00 | 69.4  | 69.4  |
| 2.00-1.00 | 92.7  | 92.7  |
| 1.00-0.00 | 100.0 | 100.0 |

D(AVE) 2.62 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



HORIBA CAPA-500  
PARTICLE ANALYZER

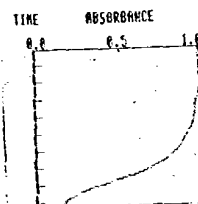
DATE 5/23/82  
SAMPLE C3-T3-T3  
SOLVENT F30

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(MAX) 10.0 (PM)  
D(MIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 8 H 4 MIN 20 SEC

• DATA

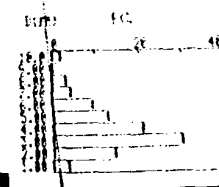


• DISTRIBUTION TABLE (BY VOL.)

| D (PM)    | F (Z) | R (Z) |
|-----------|-------|-------|
| 10.0      | 0.0   | 0.0   |
| 10.0-9.0  | 1.8   | 1.8   |
| 9.00-8.00 | 0.0   | 1.8   |
| 8.00-7.00 | 3.1   | 4.9   |
| 7.00-6.00 | 4.3   | 9.2   |
| 6.00-5.00 | 9.4   | 18.6  |
| 5.00-4.00 | 12.8  | 31.5  |
| 4.00-3.00 | 20.7  | 52.2  |
| 3.00-2.00 | 30.0  | 82.2  |
| 2.00-1.00 | 14.3  | 96.5  |
| 1.00-0.00 | 3.5   | 100.0 |

D(AVE) 3.11 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



ATTACHMENT C

IBM

YU 10179

Technical Notebook

Book V

User's Initials and Last Name:

DUNCOMBE, P.

Employee Serial:

15 5139

Date of First Entry:

6/7/88

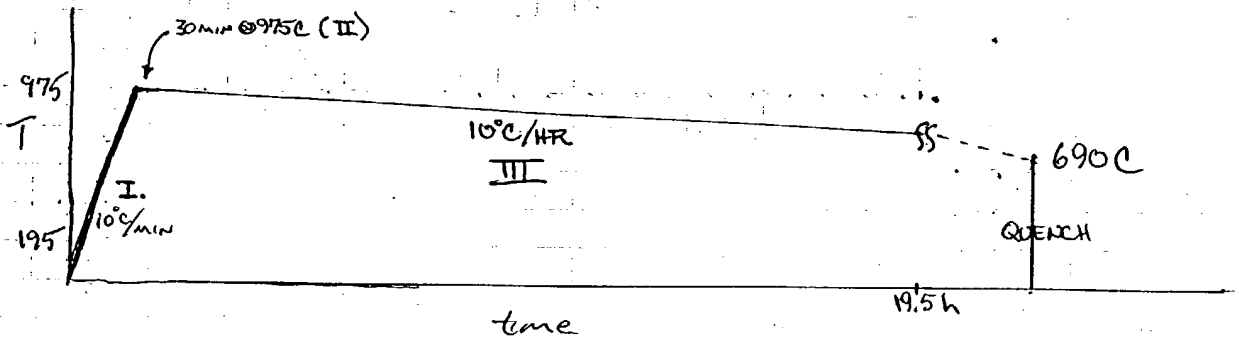
Date of Last Entry:

5/89

Security Classification:

6/7/88

# Next "transition" Heat Treatment (B)



I.  $250 - 975 \rightarrow \Delta 950^\circ\text{C} / 10^\circ\text{C}/\text{min} = 1.583 \text{ h} \text{ (1h 35 min)}$

II.  $975^\circ\text{C} \text{ for } 30 \text{ min} = 0.5 \text{ h}$

III.  $975^\circ\text{C} - 690^\circ\text{C} = \Delta 285^\circ\text{C} / 10^\circ\text{C}/\text{h} = 28.5 \text{ h}$

total:  $28.5 + 0.5 + 1.58 = 30.58 \text{ h}$

Proposed: pregtill 10 A.M. Monday  
10-11:35 am  $\rightarrow$  heat up (RAMP I)  
11:35-12:05 pm  $\rightarrow$  dwell  
12:05 pm - 4:35 pm Tuesday  $\rightarrow$  RAMP 2 (cool)  
4:35 pm Tuesday quench

(A) As B above w/  $650^\circ\text{C}$  QUENCH w/ I: as above  
II: as above  
III: 32.5 h }  $\sim 34.5 \text{ h total}$

ON @ 11:40 A.M. 6/13

START RAMP down @ 1:45 p.m. (actually 2:05)

Drop to  $946^\circ\text{C}$  @  $10^\circ\text{C}/\text{min}$  then slo RAMP to  $0.17^\circ\text{C}/\text{min}$

Estimated Quench time 25h 24min OR 3:36 p.m. 6/14/88

6/14/88  $\Rightarrow$  2:45 updated Quench TIME

3:15

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2

IBM Technical Notebook

tidbit :  
(conversion)

$$\text{mm Hg} = 0.001333 \text{ bars} \therefore 0.001333 \text{ bar/torr}$$

$$1.333 \text{ mbar/torr} \rightarrow 0.75 \text{ mtorr/mbar}$$

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502 R1

{100, 10%/min, 1550C, 61mm, 10%/min, 100C} RUN SPECS

6/29/88

IBM Technical Notebook

| T     | PV   | Proc | Man% | Ampl             | Volts | meter | <sup>mm</sup><br>ASP | Comments                |
|-------|------|------|------|------------------|-------|-------|----------------------|-------------------------|
|       |      | 100  |      |                  |       | 6.0   |                      | START                   |
| 12:20 | 986  | 990  | 10.4 | 490              | 2.5   | 6.92  |                      | 4x10 <sup>-5</sup> Torr |
| 12:42 | 1196 | 1200 | 14.9 | 600              | 3.1   | 7.11  |                      | 5x10 <sup>-5</sup> Torr |
| 12:57 | 1346 | 1350 | 20.4 | (700)            | 4.0   | 7.27  |                      | 4.6X/12 psi             |
| 1:07  | 1445 | 1450 | 25   | (725)            | 4.75  | 7.37  |                      | 3.5                     |
| 1:17  | 1550 | 1517 | 30.3 | 700              | 5.4   | 7.48  | 60.1                 | ↓ 12                    |
| 1:48  | ↓    | 1550 | 29.7 | 700<br>700       | 5.4   | 7.47  | 80                   | 3.6/12                  |
| 2:18  | 1550 | 1550 | 29.2 | 690 <sup>+</sup> | 5.25  | 7.469 | 0                    | 1.25/3                  |
| 2:32  | 1415 | 1407 | 20.3 | 625              | 4.25  | 7.34  | X                    | 8x10 <sup>-6</sup> /2   |
| 3:45  | 679  | 678  | 3.6  | 300              | 1.5   | 6.61  | -                    | 28E-6/2                 |
| 4:20  | 333  | 325  | 0    | 0                | 0     | 6.29  | X                    | 28 / ✓                  |
| 4:45  |      |      | 0    | 0                | 0     |       |                      |                         |

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4/5/88 STBX-2 IBM Technical Notebook

| Time   | PV   | Prog | Man%                                       | A    | V    | gauge | ASP   | Comments                        | Vac                  |
|--|------|------|--|------|------|-------|-------|---------------------------------|----------------------|
| 10:40  | 341  | 341  | 3.4  | 350  | 1.5  | 7.76  |       | bias changed @ start            |                      |
|  | 640  | 641  | 6.2  | 390  | 1.6  | 7.98  |       | 20 PSIG applied                 | $5 \times 10^{-5}$   |
| 11:42  | 962  | 961  | 8.6  | 460  | 2.4  | 8.20  |       | 40 ↓                            | $1.8 \times 10^{-5}$ |
| 1:00   | 1650 | 1650 | 35.4                                       | 735  | 6.0  | 8.88  | 112.0 | ✓                               | $1.9 \times 10^{-5}$ |
| 2:30   | ↓    | ↓    | 35.3                                       | 725  | ↓    | 8.86  | 22.8  | ∴ 2:52                          | $2.5 \times 10^{-5}$ |
| 3:00   | 1576 | 1565 | 28.0                                       | 700  | 5.5  | 8.78  | —     | → 2:53                          | $1.8 \times 10^{-5}$ |
| 4:45   | 532  | 530  | 2.5  | 360  | 1.75 | 7.87  | —     | load removed (9 PSIG)           | $4 \times 10^{-6}$   |
| 5:07   | ~300 | ~300 | 0.8  | <300 | <1   | 7.70  | —     | increase flow to 8.5 gpm from 7 |                      |
| 5:10   |      |      |  |      |      |       |       | STOP STOP                       | $1.6 \times 10^{-6}$ |
| 5:15   | 200  | 228  | off  | —    | —    | 7.61  |       | SHUT OFF H2P                    |                      |
| 5:20   | 149  | 162  | —  | —    | —    | 7.52  |       | vacuum constant ~12.5 PV/min    |                      |
| started backfill (5122 STP on mech gears, light out), mech shut down, high vac closed. |      |      |  |      |      |       |       |                                 |                      |
| 5:25   | 178  | 134  | GAS has RAISED temp, but Ar. GPM up to 18. |      |      |       |       |                                 |                      |
| 5:30   | 2140 | 100  | Prog off                                   |      |      |       |       |                                 |                      |

Notes: 300 C @ 10:36 ∴ 2h 15m to S.P. ⇒ 12:45 (est) + 2h ⇒ 2:45 Ramp down  
 ~3.5 hrs for cooling, <100C opening @ 6:15 approx (due to thermal mass lag)

Unsuccessful. Some sticking to bottom foil. Cracked with diffusion zone and multiple phase boundary.



6/28, B.1/C

Ar/H<sub>2</sub> Bi 20 { Bi 25 pieces remaining after slicing isostatically pressed to 28,000 PSI at

Bi 25 → some obvious large void improvement on at least 1/2

Bi 20 → possible visible evidence of compression, need to section. (especially large 1/2)

Objectives:

1) isopress as above

2) slice

3) anneal remaining sections

4) study wetting/densification vs temperature relationship

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6/7/77 STBX-3

| Time   | TV   | Proy | M%   | A   | V   | quadr | $\Delta SP$ |
|--------|------|------|------|-----|-----|-------|-------------|
| ~11:00 | 42   | 427  | 35   | 350 | 1.5 | 7.69  |             |
| 11:58  | 1004 | 1006 | 9.2  | 490 | 2.5 | 8.23  |             |
| 11:02  | 1576 | 1575 | 29.5 | 675 | 5.5 | 8.82  | 122         |
| 1:25   | 1575 | 1575 | 29.3 | ↓   | ↓   | 8.81  | 91.6        |
| 2:45   | 1575 | 1575 | 29.2 | 675 | 5.5 | 8.80  | 15          |
| 4:45   | 599  | 599  | 0.0! |     |     |       |             |

~~STBX~~

7

Comments  
 est. S.P. start: 1:17, SE-6  
 1.8E-5  
 ↓ est. ~ 3:00 start ampelur  
 1.0E-5 → 9.6E-6  
 7.5E-6  
 Different than last run, even on 7gpm!

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Date

and

Date

7/11 2050 Bake out Pre Al<sub>2</sub>O<sub>3</sub> : I 88 [Reg 8]

7

| Time  | TV   | Proc                  | M%   | At   | V   | gtr        | $\Delta$ SP | Vac    | Comments   |
|-------|------|-----------------------|------|------|-----|------------|-------------|--------|--|
| 12:30 | 1660 | 1687                  | 40.1 | 760  | 6.4 | —          | —           | 5E-5   | Ramp 20%/min. : 1200C/hr<br>Some degassing > 1650    |
| 12:42 | 1893 | 1935                  | 66.2 | 900  | 8.4 | —          | —           | 4E-4!  | Agpm   |
| 12:52 | 2037 | 2050                  | 88.7 | 950  | 9.5 | —          | 10/5        | 7E-4   | definitely 'baking out'<br>top was 2040 (over 5 min) |
| 12:55 | 2028 | 2003                  | 84.4 | ✓    | ✓   |            |             |        | Hold to continue B-out                               |
| 1:00  |      |                       | 92.0 |      |     |            |             |        |  |
| 1:04  | 2061 | H                     | 96.0 |      |     |            |             | 4E-4   | Raised manually<br>PV steady ↓ agpm                  |
| 1:11  | 2083 | H                     | 98.0 |      |     |            |             |        |  |
| 1:17  | 2094 | H                     | ↓    | 1000 | 10  | —          | —           | 3E-4   | Holding  |
| 1:34  |      | same                  |      |      |     |            |             | 1.9E-4 | Vac increasing as hoped                              |
| 2:05  | 2092 | same                  |      |      |     |            |             | 9E-5   |  |
| 2:30  | 2093 | switched back to Auto |      |      |     |            |             | 6E-5   | Start TV ramp down                                   |
|       | 2093 | 2000                  |      |      |     |            |             |        |  |
| 2:46  | 1727 | 1691                  | 38.9 | 790  | 7.5 | —          | —           | 2E-6   | Good vac for 1800C RUN                               |
| 3:20  | 1004 | 1000                  | 6.7  | 475  | 2.5 | —          | —           | 9.8E-7 |  |
| 3:45  | 572  | 520                   | 1.0  | 200  | 0.0 |            |             | 8E-7   |  |
| 4:10  | 255  | off                   | —    | —    | —   | STP300 off |             | 7.5E-7 | up to Agpm from 7                                    |
| 4:30  | 138  |                       |      |      |     |            |             | 3.5E-4 | STP shut down to mesh bearings                       |
| 4:33  |      |                       |      |      |     |            |             |        |  |
| 4:38  |      |                       |      |      |     |            |             |        |  |

Argon flush after ion shut off  
 melonced off

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8

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# SET-UP For I88 $Al_2O_3$ BYSTAL IBM Technical Notebook

9

| SEG | Temp<br>(°C) | time<br>duration | Ramp Rate<br>(°C) | SEG<br>time            | Psig                     |
|-----|--------------|------------------|-------------------|------------------------|--------------------------|
| 01  | 100°C        | 0.1              |                   | <del>1h</del> 3h       | apply initially 100      |
| 02  |              |                  | +600/h            | 2h 50m                 |                          |
| 03  | 1800C        | 5.1              | 566.7             | 5h                     |                          |
| 04  | 1400         |                  | 60 - 12/h         | 6.7h                   |                          |
| 05  | 100C         | 0.1              | 80                | 16.25                  | remove load @ start ramp |
| 06  |              |                  |                   | 21.25                  |                          |
| 07  | 100C         |                  |                   | NET 2.5h save 23 total |                          |

Time factors: start @ 10:00 A.M., seg 01 begins ~ 5:00 p.m.  
seg 05 ends ~ 5:30 p.m. next day O.K.

Pressures from 2/13/87 (Book II pg 49 notes)

$$P_s = \frac{Area_{ref} (P_g)}{A_{spec}} : \text{ref - ram x section } (4.9") \quad P_g - \text{gauge spec + specimen}$$

Psig of 180 for Bxstal Run 87III resulted in yield of moly stage and XTAL indentation. So, in lieu of carbon stage switch not possible at moment, will approx. have pressure to 100 psig and apply load initially, releasing after ramp down begins. This worked fairly well with Doane's  $SiTiO_3$  and similar 87III run yielded only partial cracking of samples

$$P_{sample} = \frac{(4.9) (100)}{(0.221)} \approx 2210 \text{ versus article (ref) max of } \sim 4200 (60\%)$$

$$\sim 2225$$

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10/14 I 88 Bxstal Run IBM Technical Notebook

| Final<br>SEG | Prog<br>T <sub>1</sub> | t<br>duration | °C<br>Rate | seg<br>time | Psig |
|--------------|------------------------|---------------|------------|-------------|------|
| 01           | 100C                   | 0.1h          |            | 6min        | 110  |
| 02           |                        |               | 60/h       | 2.8h        | 110  |
| 03           | 1800C                  | 4.75h         | -          | 4.75h       | 110  |
| 04           |                        |               | 80/h       | 21.25h      | NOM. |
| 05           | 100C                   |               |            |             |      |

1.4-4.0E-5 torr  
 NOTE: intermediate 60/h ramp skipped  
 due, however temp fell from ~1790  
 to 1730 in overshoot before 80/h  
 ramp kicked in. 4E-5-8E-7

Run notes: @ ~7:00 pm 7/13 TC peak noticed during inspection.  
 repaired as possible. Seems to have taken up. See note  
 above.

Results: Severely cracked xstal. Some sticking, but no rxn. with  
 Mo shim on stage, but carbon/Mo rxn from top ramp/shim  
 couple. Pitting/roughing top surface / likely initiating  
 cracks.

The above understood

Date

and

Date

WRAP-UP George's Bi/Cu work IBM Technical Notebook

Try 10g batch

2.5g Bi 7.5g Cu use

2.48 tare  
12.49 after tare

Also took 1/2 20 & 25 Bi Ag/Hg(5) Run isostatically  
pressed forms AND will Anneal while sintering bar.

To Lamp @ 3:00 p.m. 7/25/88 18h → 9 A.M. 7/26/88

4:20 p.m. 7/25/88 → new type D {25Re/W3Re}

thermocouple seems stable as well as 818 programmer  
@ 750C

9.99(8) 4.060

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# IBM Technical Notebook

## III. DENSITY WORKSHEET

### STEREOPYCNOMETER TRUE POWDER DENSITY

SAMPLE I.D. \_\_\_\_\_ DATE 7/26/88  
 SOURCE 258/Lw Bar OPERATOR PPD  
 TOTAL WEIGHT 13.981 g. OUTGASSING CONDITIONS \_\_\_\_\_  
 TARE WEIGHT 4.060 g.  
 SAMPLE WEIGHT 9.921 g. ADDED VOLUME,  $V_A$  85.52 cc  
 CELL HOLDER VOLUME,  $V_C$  34.85 cc

$$\text{OPERATIONAL EQUATION } V_P = V_C + \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_P$  = Volume of Powder (cc)  
 $V_C$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$   
 $P_2/P_3$  = 3.5415 DATA 3.5429 3.5419

|         | RUN 1                  | RUN 2                  | RUN 3                     |
|---------|------------------------|------------------------|---------------------------|
| $P_2$   | <u>19.457</u>          | <u>19.656</u>          | <u>19.746</u>             |
| $P_3$   | <u>5.494</u>           | <u>5.548</u>           | <u>5.575</u>              |
| $V_P$   | <u>1.2006</u> cc       | <u>1.219</u> cc        | <u>1.206</u> cc           |
| DENSITY | <u>8.2634</u> g/cc     | <u>8.1316</u> g/cc     | <u>8.23</u> g/cc          |
|         | <u>8.26/9.17 = 90%</u> | <u>8.14/9.17 = 89%</u> | <u>8.23/9.17 = 89.75%</u> |

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Average: 89 + 89.75 ≈ 89.5 Between 89-90%

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IBM Technical Notebook

13

A. Liq.  $\phi$  Bi/Cu System Development Summary  
 Initial compositions: Conditions: 400C in  $N_2$  overbite  

| % Bi (liq) | % Cu (solid) |
|------------|--------------|
| 1          | balance      |
| 3          |              |
| 10         |              |

NOTES: CONDITIONS AND % comp. Bi did not lead to desiccation (sintering) of plugs. No sight loss. 5g samples in vitreous carbon crucibles

B. %Bi %Cu Conditions: 750C in  $N_2$  overbite  

| % Bi | % Cu    |
|------|---------|
| 50   | balance |
| 10   |         |
| (3)? |         |

NOTES: nothing in  $N_2$  does not seem to be total, possibly oxide films interfering behavior. 50/50 mix too much liq. Sur products apparent. 10% too little liq. No appreciable weight loss.

E. %Bi %Cu Conditions: 'packed' pure crucible  

| % Bi | % Cu    |
|------|---------|
| 25   | balance |

  
 'Face' under @ 750C overnight in  $Ar/H_2$ . No composition (grey)

NOTES: Porosity is reduced, 3rd  $\phi$  oxide has been eliminated in forming  $\phi$ , nothing seems approx complete. Little difference between 100 mesh spherical Cu and 10  $\mu m$  Cu, though 10  $\mu m$  seems to give better overall results. Reactions RUN seems to need more time, but nothing characteristics seem better. Will re-run sample as next run (i.e. 2x overbite)

F. Vacuum 25 Bi Run

conditions: highly porous. Vacuum doesn't appear to work well in  $Ar/H_2$ . No evidence of oxidation, however, indicating vacuum was O.K. No evidence of vapor phase deposits, even in glass tube.

C. %Bi %Cu Conditions: 750C in  $N_2$  overbite  

| % Bi | % Cu    |
|------|---------|
| 25   | balance |
| 35   |         |

NOTES: ~ density 25 Bi (90)  $\phi$  61.4 g/cc (assume 1.17 g/cc for 25% fully dense body). Definitely bead-like, rounded edges, or dense. 35% Bi density not calculated but films obviously smaller  $\therefore$  sample density is at least same or higher. Still evidence of incomplete wetting. Must then  $\phi$  evident of possible oxide?

D. Compressed pellet run Conditions: 750C in  $Ar/H_2$  overbite  

| % Bi | % Cu    |
|------|---------|
| 25   | balance |

NOTES: ~ calc density 25 Bi pressed (79%) porous basis. Evidence of better wetting, sintering and assumption still previously. Low density due to pellet bloating, probably trapped air in pores. No significant Bi vaporization evident by weight loss.

G. %Bi %Cu Conditions: 'packed' pure crucible  

| % Bi | % Cu    |
|------|---------|
| 10   | balance |
| 20   |         |
| 25   |         |

  
 sintered @ 750C overnight in  $Ar/H_2$ . No composition.

Results: Good areas and wetting with 20 & 25% samples, however 20% seems better overall with small air born pores whereas 25% has some voids as well as pores.

20 & 25% Bi samples pressed to 27,500 psi isostatically. Some collapse of large porosity/voids. Little effect on small porosity.

Appending effect: 0.02 & 0.04 g of Bi-each liq. ran out of microstructure upon melting. Porosity diminished. Very good looking relatively dense 20% sample.

'Base': 25% Bi (10g lumps) in vitreous boat first placed in house vacuum (desiccator) then sintered overnight per std. treatment producing very good looking microstructure with little porosity.

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Date

8-11-88

GREEN phase - substrate work

Get not found from memory

have one remaining substrate, ~80-90% dense, single phase, sinter T 1350C

① pressed 0.2", 0.2g pellet of eutectic

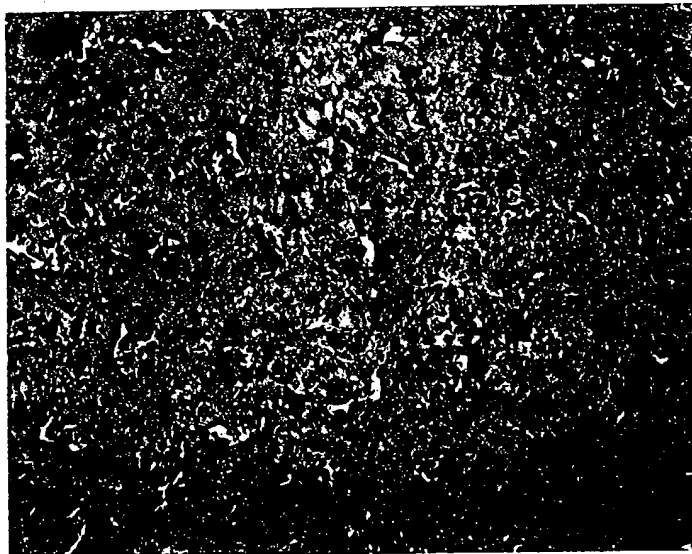
8-18-88 week summary

1500C pellet almost totally melts (2 $\phi$ ) with interaction between <sup>211 coarse "off comp"</sup>  $Al_2O_3$  and liq.  $\phi$ .

1400C pellet retains ITS INTEGRITY, BUT large amount of LIQ forms 2 $\phi$ , interaction w/ liq  $\phi$  and support

1350C liq  $\phi$  still present, though diminished. less interaction. for short sinter time  
211 milled "on"

1315C 211 1H 100X milled powder



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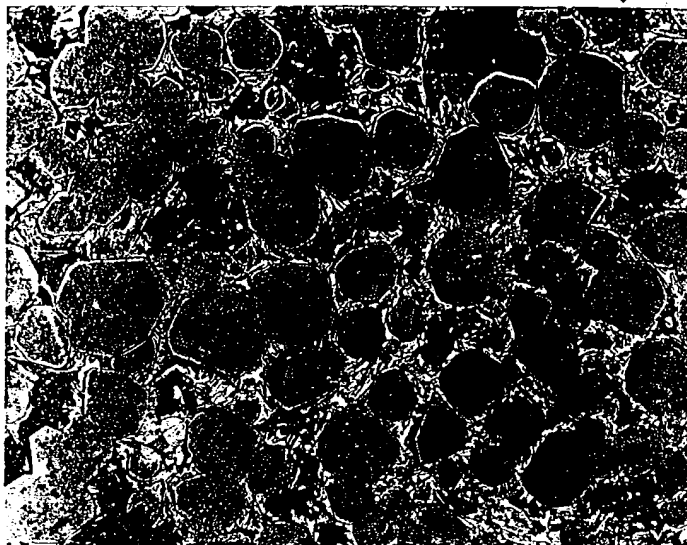
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1292C 18HRS 211 milled

100X



1265C 'excess' 'offcomp' overnite

100X



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211 milled 1235C 2HRS 1000X



Conclusion: sintering @ 1292C or higher creates 2x material exaggerated liq & grain growth after prolonged period  
sintering @ 1235C does not induce adequate sintering. pellet REMAINS green as opposed to higher temp, where pellet turns black (presumably this is not simply surface effect, but has chemical basis)  
sintering @ 1265C may be optimal.  
Purity definitely too?

18 Green density - 211m 0.6 pellet  
 5500

2.56 1.548 0.399 0.7509 3.41 / (6.36) = ~50%

150

✓ 1.472 0.389 0.662 3.87 / (6.36) ~ 60.9

(6.00) ~ 64.5

Post → pellet not good enuf to bother. 2φ, stuck, etc. (1292C) 18H

1265C pellet II (150 29)

2.56 1.457 0.398 0.66 3.88 / (6.00) ~ 64.5

pellet cracked on checking must REPO, temp O.K. though (1265C)

pellet III w furnace @ 4:10 to temp @ 4:30

set 1255, T<sub>sample</sub> ~ 1270

2.53 1.286 0.360 0.47 5.38 / (6.00) ~ 89.7%

8/23/88 15029, pellet IV (second 'good')

2.81 1.455 0.438 0.7283 3.86 ~ 64.3%

8/26

2.8 1.283 0.384 0.4964 5.64 ~ 94

15030, pellet IV (edge chipping during isopressing) O.K.

2.94 1.456 0.457 0.761 3.86 ~ 64.4% consistent

4:20 to temp @ 1267C

2.93(5) 1.283 0.4- 0.517 5.67 ~ 94.5 ~ 65h

2A

3 good slices

8-31

0.04g 0.33mm dia pellet set on edge of polished 211 substrate which itself rests on a piece of 211 resting in a  $Al_2O_3$  boat on a bed of 123. Adjacent to substrate is small pellet of 211 to allow eutectic pellet to straddle edge of substrate to minimize contact.

Heat treatment:  $10^\circ C/min$  to  $1000C$  in flowing  $O_2$

previous exps. in air/ $O_2$  showed incongruent melting of eutectic @  $\sim 1000C$ .

10:45 A.M.  $T @ 500C$   $\therefore 1000C$  plateau should be reached @ 11:35

Will allow to melt for 1h  $\rightarrow 12:35$

$10C/min \rightarrow 725$  1:00

$5C/min \rightarrow 600$  1:30 hold

~~10C/min~~  $\rightarrow$  ~~good 2:30~~

$\rightarrow 10C/min \rightarrow 300C$  quench

Flow not pronounced. Not alot of liq. formation. Pix taken.

Re-do in Air/ $O_2$  where prev. exp. showed alot of liq. formation.

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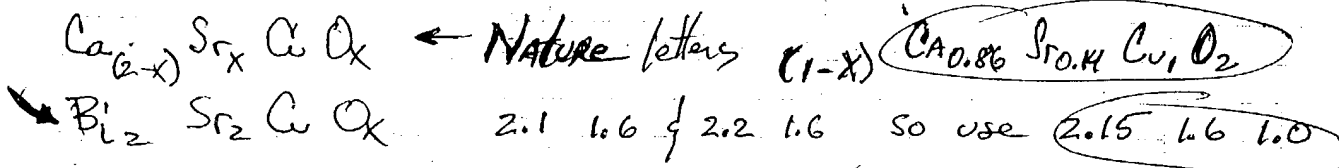
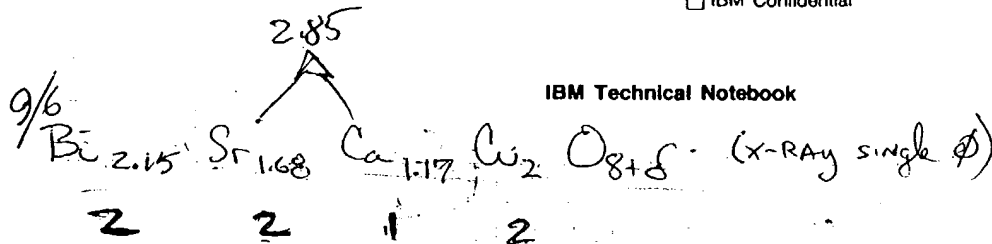
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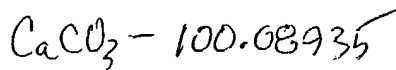
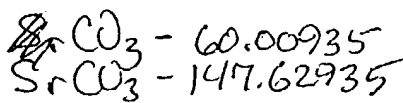
Date





|    |         |                          |   |
|----|---------|--------------------------|---|
| Bi | 208.980 | $\text{Bi}_2 \text{O}_3$ | <del>465.9582</del> 465.9582 g/m (2 moles!) |
| Sr | 87.62   | $\text{SrO}$             | 103.6194                                    |
| Ca | 40.08   | $\text{CaO}$             | 56.0794                                     |
| Cu | 63.54   | $\text{CuO}$             | 79.5394                                     |

|                                     |               |                               |           |
|-------------------------------------|---------------|-------------------------------|-----------|
| 2.15 moles $\text{Bi}_2 \text{O}_3$ | 1.00181013 g  | 150 $\rightarrow$ 150.2715195 | 2.2 76.58 |
| 1.68 $\downarrow$ $\text{SrO}$      | 0.17408059 mg | 26.1120885                    |           |
| 1.17 $\text{CaO}$                   | 0.06561290 mg | 9.841935                      |           |
| 2.0 $\text{CuO}$                    | 0.15907880 mg | 23.86182                      |           |
|                                     |               | 210.087363 g                  |           |



$\frac{\text{SrCO}_3}{\text{SrO}} : \frac{147.62935}{103.6194} = 1.42472693 (26.1120885) = 37.20259576$

$\frac{\text{CaCO}_3}{\text{CaO}} : \frac{100.08935}{56.0794} = 1.78477926 (9.841935) = 17.56568146$

IBM Technical Notebook

229/6

- ① Mixed, ground and calcined @ 775C 21 h (PE)
- ② Gnd kept in  $Al_2O_3$  boat covered w/ Au foil  
 ③ 800C for 6 h
- ③ Gnd and recalcined @ 850C for 16h
- ④ Gnd & mill for pelletization

Factor of 2 molar correction

18.78393994 g

$$150.2715195 / 4 = 37.56787988$$

37.20259576

$$9.30064894 (0.70188889) \approx 6.528$$

17.56568146

$$4.3142037 (0.56029328) \approx 2.41605$$

23.86182

5.965455

57.22540 ~~(0.70188889)~~

- 1.931

- 2.7726

52.522 g batch

scale up everything by 1.5

28.176

13.950

6.587

8.948

57.661 (less  $CO_2$  loss\*)

$$13.95 (0.70175) = 9.7895$$

$$6.59 (0.560) = 3.69$$

4.16 g loss

2.9 g loss

7.06 total expected

|                 |                  |                  |  |   |
|-----------------|------------------|------------------|--|---|
| 9-7<br>$B_2O_3$ | calc'd<br>28.176 | weigh'd<br>28.18 | IBM Technical Notebook<br>GRAV REC<br>207.28 ← bottle tar<br>235.45<br>28.17 | 23<br>post<br>207.30(1)<br>$\Delta + 0.03$<br>207.27<br>0.05%<br>loss |
| $SiO$           | 13.950           | 13.96            | 235.45<br>249.41<br>13.96  |   |
| $CaO$           | 6.587            | 6.59             | 249.41 (2)<br>256.02<br>6.61 + 0.01(2)!                                      |   |
| $CuO$           | 8.948            | 8.96             | - 0.01(2) recovery better<br>6.60<br>256.00 (0.02)<br>264.96<br>8.96         |   |

- ① Pwd. transferred to O.D. tall bottle, shaken for > 15 mins.
- ② to 400ml beaker w/ ~150ml (made up to) 150
- ③ Continuously stirred w/ mag. stirrer while removing solvent. 11:30 → 1:20
- ④ Stirrer removed lowered to 'low', dry for over @ 2:00  
In oven under vac @ "3" 2:05 → 3:45

146.59 (8) beaker 159.46  
 89.12  
 57.47 vs 57.69 (0.4% loss) may be some

152.23 (2) w/ top

146.59  
 142.15 post 20 NO EVIDENCE OF VAPOR  
 4.44 g loss ⇒ 7.06 g expected @ 63% conversion if no Br loss  
 89.12  
 53.03 ~51.26 52.86 ne 99.7% > Post gnd 51.43 97%

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B<sub>1</sub>SrCaCu Calorization II: gold lined Al<sub>2</sub>O<sub>3</sub> boat

86.51 barely fits in larger boat  
35.13

51.38 vs 51.43 0.1% transfer loss

85.10  
35.13  
49.97

49.34 In furnace (tube) for 850C, 16h calorization

84.50(48)  
21 stuck in screen  
84.71

83.58  
35.13  
48.45 post 850C 16h calorization  
need on X-RAY

IBM Technical Notebook

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9-7  $B_{2.15} Sr_{1.6} Cu_1 O_x$  (ref. data pg 21)

2.15 moles  $B_{12}O_3$  1.00181013 ~~but~~  $2Bi = 1B_{12}O_3 \cdot 2$

$Bi$  0.50090507 mg/mm

1.6 moles  $SrO \rightarrow (1.6)(103.6194) = 0.16579104$  mg/mm

1.0 mm  $CuO \rightarrow$  = 0.0795394

$SrO \rightarrow SrCO_3 \rightarrow 1.42472693(0.16579104) = 0.2362(0696)$

scale factor for 50g lot  $\sim 60$

(60) (0.50090507) = 30.0543  $Bi$   $u_x$

(0.23620696) = 14.1724  $Sr$  as  $SrCO_3$

(0.0795394) =  $\frac{4.7724}{48.9991}$   $Cu$   $\sim 49g$  close enough

$Ca_{0.86} Sr_{0.14} Cu_1 O_2$

0.86 (56.0794) = 0.048228284 (1.785) = 0.0861

0.14 (103.6194) = 0.014506716 (1.42472693) = 0.02066811

1.0 (79.5394) = 0.0795394

scale factor for 50g batch (340)

340 (0.048228284) = 16.398

(0.02066811) = ~~4.932~~ 7.027 (4.949)

(0.0795394) = 27.043

50.468 g (less  $O_2$ )

~~2.078~~  
48.39

29.27

7.028

27.04

63.34

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$\text{SrCO}_3$  decomp. @  $1340^\circ\text{C}$   
 $\text{B}_{12}\text{O}_3$  melt @  $880^\circ\text{C}$   
 $\text{CaCO}_3$  decomp  $825^\circ\text{C}$   
9/3 From Chandra: } all below initial calcination  $T^\circ$   
775C

$\text{B}_{1.25}\text{Sr}_{1.6}\text{Ca}_1\text{O}_x$  procedure for calcination - all Pt.

752C for 6h ← Grd. ✓

790 C overnite (16h)

~~(leave)~~

825C 16h NOT converted

890C

< 855 20h

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and witnessed by \_\_\_\_\_

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by \_\_\_\_\_

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1423 8000  
 223 27  
 111501 8250

9/8  
 ①  $B_{0.2.15} Sr_{1.6} Co_1 O_x$   
 $B_2O_3$  30.0543 30.06  
 $SrCO_3$  14.1724 14.18  
 $CoO$  4.7734 4.78  
 $\frac{.999}{.999} = 4.777 \rightarrow$

201.50 tare  
 231.54  
 30.05 ✓  
 241.72  
 14.17 ✓ (9.98 oxide)  
 250.90 (49)  
 4.78 ✓ ✓ OK.

$Co_{0.86} Sr_{0.14} Co_1 O_x$   
 $CoCO_3$  16.398 16.40  
 $SrCO_3$  2.027 2.03(4)  
 $CoO$  27.043 27.04  
 $\frac{27.043}{.999} = 27.07$

211.32 (3) tare  
 227.74 (2-6) ③  
 16.42 recovery } slightly  
 234.79 } unstable  
 2.03  
 261.81  
 27.04 ✓  
 2.03 added  
 27.07

Shaker, suspended in iso, mixed & dried as per 2212 previously.

Will start both tomorrow after consultation w/ R. Figg.  
 Mend says try 8000 to start in Pt.

No-transfered to HCl cleaned B.SrCo crucible & fired for 6 h overnight.

137.87  
 89.15 tare (89.12) 0.03 exp.  
 48.72 / 49. expected 0.28/49 =  
 135.86 Post 6 → Greenish yellow (46.71)  
 -Δ2.01 (/4.19 expected) 48% reacted  
 135.51 (46.34)

28

IBM Technical Notebook

133.28  
133.66

Calculation II (post grand #1)

B.S.C.

$$\begin{array}{r} 135.51 \\ - 89.15 \\ \hline 46.34 \end{array} \quad -\Delta 0.37 / 46.71 \quad (0.8\% \text{ loss})$$

$$\begin{array}{r} 133.66 \\ - 89.15 \\ \hline 44.51 \end{array} \quad \text{post } 790^\circ\text{C } 16\text{h brownish-black hue, little sintering}$$

44.10  
132.66 let stand overnight. will run x-ray in morning.  
post 825°C 16h rich black texture, little sintering  
exterior of sinter mass (tan?)

CONT pg 30 →

Calculation II ~~Sn-Cu~~ ~~pg 23~~

$$\begin{array}{r} 140.92 \\ - 90.48 \\ \hline 50.43 \end{array} \quad / 50.52 \quad 0.03\% \text{ loss}$$

$$\begin{array}{r} 16.42 (0.56) = 9.1952 \quad (-\Delta 7.225) \\ 7.03 (0.702) = 4.935 \quad (-\Delta 2.095) \\ \hline - 9.32 \end{array}$$

$$\begin{array}{r} 133.28 \\ - 90.49 \\ \hline 42.79 \end{array}$$

$$\begin{array}{r} 50.48 \\ - 9.32 \\ \hline 41.20 \end{array} \quad \therefore 42.2 / 42.8 \quad 96\%$$

42.43 post grand 0.8% loss. {Product looked good, little sintering, black.}

$$\begin{array}{r} 132.90 \\ - 90.49 \\ \hline 42.41 \end{array}$$

In furnace for 16h @ 1000°C. Partial melting.  
9/13 Run aborted. Restart. Cal I @ 800°C then x-ray.



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9/13  $Ca_{0.88}Sr_{0.14}Co_1O_x$  RESTART // melting @ 1130 want  
1,000W experimental synthesis  
XSTALS excited Chandra. Same formula over.

9/4  $CaCO_3$  16.398 16.41 227.76  
211.35 (4) tare  
16.41  
 $SrCO_3$  7.027 7.04 234.80  
7.04  
 $CoO$  27.07 27.07 261.84 (5)  
27.04 (5)

9/15  
Run shot due to  
bump prog when  
someone turned up  
heat

#3  
 $CaCO_3$  16.41 2  
211.45  
227.85 (6)  
16.40 (4)

$SrCO_3$  7.04 227.86  
234.90  
7.04 ✓

$CoO$  27.07 261.96 (7)  
27.06 ✓✓

#4- 9/21/88  
 $CaCO_3$  16.41 211.49 (±1)  
227.88  
16.40

$SrCO_3$  7.04 234.92 (±1)  
227.89

$CoO$  7.03 ✓  
261.98 (9)  
27.06 ✓

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and  
by \_\_\_\_\_

Date \_\_\_\_\_

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30 One last time 9/21

CaCO<sub>3</sub> 16.41

227.88 (9)

211.48 ~~211.48~~ HARE (+1)

16.40

PrCO 7.04

~~234.98~~

227.89

7.04

CO<sub>2</sub> 27.07

262. (61.99)

234.93

27.06 ✓✓

Gold for Dick

22.87 g rev

3.92 owed

13.95 remaining

8.92

5.88 returned

3.04 returned

VACATION ⇒ 9/26 ~~15/24~~ 23, 22/88

After drying (n days) ~~we send~~

138.94

89.15 (14)

49.79 g recovered / 50.5

0.21/50.5 1.4% (bumping, etc)

VACATION 9/28, 29, 30/88

Post I 138.94

131.15

7.79 loss

131.15

89.15

42.00 g net

II finish

40.3 g collected after grinding for possible cal III

TO PAGE 32

PRE II

131.07

89.17

POST II 129.66

89.16

40.00

40.52

9.79 g loss

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$B_{2.0}$   $B_{2.1}$   $B_{2.2}$

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9/14

43 g  $B_{2.15} Sr_{1.6} O_x$  collected after 16h 825C cal.  $\{ < 100$  mesh g.  
will await X-ray tomorrow morning  
Set-up jet mill. Pick still busy w. X-ray.  
9/19

10/3

Definitely NOT CONVERTED! X-RAY RUN.

10/4

Calculation II - 850C 20h

RE  $\begin{array}{r} 132.13 \\ 89.12 \\ \hline 43.01 \end{array}$  Est  $\begin{array}{r} 132.03 \\ 89.12 \\ \hline \end{array}$  36h total: significant sintering has occurred  
probably "wet". Minor sticking  
for crucible (Pt).  
38.93 recovery

10/6

Cal III 875C 16h

Sintered. Not very hard but has  
"metallic" luster. No melting.  
(10/7) FINAL cal. X-ray shows some small  
additional peaks, but predominantly  
"2201"

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Date

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Nominally  
 "0011"

10/4 900C melt test on partially reacted CaSrCu : 0011  
 after 875 16h pattern discernable in x-ray but multicomponent mixture. ABOVE TEST TO SEE IF 900C cal safer

$$\begin{array}{r} 126.92 \\ 86.66 \text{ tare} \\ \hline 40.26 \end{array}$$

890C seems to be temp (+5C)

10/7 Chandra says 880C may be onset. Final cal. temp suggested @ 865C

10/6 925C 16h : x-ray shows

10/7 965C 16h

$$\begin{array}{r} 126.37 \\ 86.66 \\ \hline 39.71 \end{array}$$

appears as usual, some minor sintering. Still reacting, pattern losing other peaks and increasing intensities of 0011.

966C 160h

Switch to 810 when 812 went wild. One overshoot to 1006C for < 1 minute. Doubt if sample saw it. Removes, some Pt exp on 1 side, hardly more usual, reground & replaced for weekend start. Hope for the best.

P<sub>6</sub>-6 t<sub>i</sub> = 30 t<sub>d</sub> = 10 } optimization parameters (temp.)

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33

9/15

14.04  
4.06

Stereopycnometer density 2212: 6.45 g/cc

① g tmm diam 0.0462 4.65 72% too high, correct  
 0.21(g) .2all .528  
 875C overnite melted/vaporized  
 PRE 0.27 0.283 0.518 0.0599 4.51 69.9% lower  
 Ret 0.265 0.293 0.574 0.076 3.49! 54 No way. 70h 852-5  
 yes! (11-3-88)

Sintering Temps - rapid temp

| Tset | Tcont | 1 sample   |
|------|-------|------------|
| 830  | 836   | 858        |
| 830  | 835   | 850 equil. |
| 855  | 863   | 875 equil. |
| 835  | -     | 855        |
|      |       | 851 equil. |

no sintering appreciable

incongruent melting/vaporization

no melting, looks pretty good

10/3 Analytical Results (ICP)

|                | wt %   | mol % | (theor) MIX mol % | +Δmol % |
|----------------|--------|-------|-------------------|---------|
| B <sub>2</sub> | 49.0   | 2.34  | 2.15              | 6       |
| Sr             | 15.8   | 1.78  | 1.68              | 3       |
| Ca             | 4.85   | 1.21  | 1.17              | ✓       |
| Cu             | 12.8   | 2.0   | 2                 | -       |
| B <sub>2</sub> | 208.98 | 3.28  |                   |         |
| Sr             | 87.62  | 1.38  |                   |         |
| Ca             | 40.08  | 0.631 |                   |         |
| Cu             | 63.54  |       |                   |         |

wt%-mol% conv.

13.55 theoretical wt% @ 2212

82.45  
~96.00

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34 P2 - ~4500 ISO-28,500 IBM Technical Notebook

10/4 1.17 0.095 0.278 0.262 4.465 69%

START SINTERING @ 4:00 PM Rapid temp setting 835. Should give pellet sintering temp of 855.  
 4:20 840°C prompt  $\Rightarrow$  Ts 854 } slightly lower  
 846°C Read } overshoot  
 4:30 839 was Ts 859 Reduced  
 836  
 4:50 Stable @ 856  
 8:30 AM 16h sinter check  
 10/5 1.14 1.15 0.287 0.291 (3.92)

Pellet warped, flowed (approx. dia. due to non-vertical sides) and possibly has second phase rxn on part of top surface. Peak temp as far as I saw was 859. MUST keep below 850 (or at), C.  
 PRE 0.94 1.12 ~0.21 0.21 4.48 69.5 ~OK

pellet looks good @ 852 after 20h (overwrite) Keep sintering for grain growth  
 10/10 0.90 1.23 ~0.23 0.27 3.3 51% does not make sense

NOTE: T. SHAW says people have seen such effects  $\rightarrow$  same as previous results though

B<sub>2</sub>O<sub>3</sub> 1.15 1.68 1.17 2.08 S  
 "22.12"

Analysis Results  
 pg. 33



1000X  
 120h  
 850C

# ~~10/16~~ 2212 DYNAMIC SINTERING EXPERIMENTS

35

Sintering conditions: 850-854°C in Air/O<sub>2</sub> will need to preheat furnace to achieve SHORT DURATION SINTERING TIMES.

5 (15) (30) ~~45~~ ~~60~~ minutes @ first

10/13 Pre

1.29 1.093 0.311 0.292 4.42 68.5% ONL 3,750 ISO 27,500

In furnace 10:26 ~ 750 T<sub>stage</sub> 11:04 out (38 over)

10:30 840

10:33 851

Start T<sub>sinter</sub> count (855-852)

Post

1/2 1.27 1.142 0.326 0.33 3.85 60% → 59.7

10/13 Pre

1.19 1.095 ~ 0.288 0.27 4.41 68.4

In furnace 12:52

~ 800 T<sub>stage</sub> (plate only)

(20 over)

12:56

850

(prompting by up to T<sub>st</sub> 865)

12:56

850

~ 852/3

Δ 15 → ~ 48/102/115

1:01

854

Post

1.17 1.131 ~ 0.296 0.297 3.74 61% → 61.1

PRE ~ (1.1)

5 1.13 1.098 0.27 0.257 4.4 68.2

Post

1.11 ~ 1.108 0.271 0.261 4.25 65.9

2:32 → IN

2:34 → START } 853

2:39 → OUT } ± 2

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36  
10-13

1.2 g irregular pellet of pure "0011" isopressed to 27,500 psi  
and sintered for microstructural investigation @ ~972C.  
→ Powder does not pelletize well @ all.

~2.h @ 972C 2φ

Post  
"2201"

1.21g 1.045 0.233 ~0.2 6.05 2hs 875 (peak 880C)

6.05/7.20 = 84%



NO PRE DATA

8-14-88  
201-1

Post polishing data recheck

1.04 ~1.046 0.200 0.172 6.05 2hs ✓



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10-18

0011 Synthesis

$\text{SrCO}_3$

theor.  
7.027

weigh 's  
7.04

$\left[ \begin{array}{l} \text{if } 0.88 \\ 6.03 \\ 29.95 (\Delta = 0.68) \end{array} \right]$

$\text{CaCO}_3$

29.27

29.28

$\text{CO}$

27.04

27.05(4)

$\text{CaCO}_3$

240.77

tare

211.48

29.29 ✓

$\text{CO}$

267.80

240.77

27.03 ✓

$\text{SrCO}_3$

274.85

267.80

7.05 ✓

after mixing & drying:  $63.15 / 63.37 = \sim 0.3\%$  loss

Pre CAL I

149.62(1)

tare

86.46(7)

63.15 ✓

Post 1ch 875C

134.56(7)

8.46(7)

48.10

$29.29 (0.5603)^x = 16.41$

$7.05 (0.7019)^x = 4.95$

$27.03 (1) = 27.03$

48.39

x pg 21

n/ top  
4

188.03

38.42

(Add to acid)



$\text{O}_2$  conv.:  $48.1 / 48.39$  looks complete

total

Pre CAL II

134.47

86.63

47.84

$(47.84) / 48.1 = 0.5\%$  gdwg loss (to temp 966 @ 4:00 p.m. 10-19-88)

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10-19-88  
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Note: 810 optimized process parameters

$P_0 = 4$   $t_i = 15$   $t_j = 5$   $AP = 2.0$

Bi Synthesis  
 Series #1

|   | 2201      | 0011      | 2212      |
|---|-----------|-----------|-----------|
| B <sub>i</sub>  | +3%       | -         | +8.84%    |
| S <sub>c</sub>  | -6.25%    | -7.1%     | +5.95%    |
| C <sub>a</sub>  | -         | -4.5%     | +2.6%     |
| C <sub>u</sub>  | ✓         | ✓         | ✓         |
|   |           |           |           |
| ⊗ estimated: 0.821/0.86 t: normalized to C <sub>u</sub> |           |           |           |
| act (1725)  |           |           |           |
|   |           |           |           |
| B <sub>i</sub>  | 2.22/2.15 | -/-       | 2.34/2.15 |
| S <sub>c</sub>  | 1.5/1.6   | 0.13/0.14 | 1.78/1.68 |
| C <sub>a</sub>  | -/-       | 0.82/0.86 | 1.2/1.17  |
| C <sub>u</sub>  | 1         | 1         | 2         |

Variances

## ANALYTICAL Results

|                | 2201                   | 0011        |      |             |
|----------------|------------------------|-------------|------|-------------|
|                | <del>theoretical</del> | theoretical | act  | theoretical |
| B <sub>i</sub> | 2.21(5)                | 2.15        | —    | —           |
| S <sub>r</sub> | 1.5                    | 1.6         | 0.13 | 0.14        |
| C <sub>a</sub> | —                      | —           | 0.46 | 0.86        |
| C <sub>u</sub> | 1                      | 1           | ✓    | 1           |

⊗ Note: C<sub>a</sub> concentration off due to omission of oxide to carbonate conversion factor in initial calculations. This is consistent with large amount of CuO second pass.

|                |      |      |
|----------------|------|------|
| 2212           |      |      |
| B <sub>i</sub> | 2.34 | 2.15 |
| S <sub>c</sub> | 1.78 | 1.68 |
| C <sub>a</sub> | 1.2  | 1.17 |
| C <sub>u</sub> | 2.0  | 2 ✓  |

The above understood

Date

and

Date

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10-26 0011 milled (10/25), X-ray indicates ~ single  $\phi$

die body : 0.483" / 1.228 mm I.D.

@ 8,500 psi puck press too fragile to go in iso. left after a few attempts @ pressing w/ resultant crumbling.

Next time : ~ 3,600 psi  $\Rightarrow$  16,000 may need to reindex, PSD not available presently.

Pre data not taken:

POST : 875C for 3h (peak 5mm @ 886C) Rapid temp find  $\phi$  (948)

1.36<sup>+</sup> (pellet damage  $\Rightarrow$  ~1.4)

3.68/4.88 = 75.6  $\Rightarrow$  76 (damage)

1.174

0.352

0.381 cc

3.675

NEED pycnometer density.

Sintered microstructure reveals ~ 80-85% dense pellet w/ minor 1-2% probably  $\text{CuO}$  phase in some triple points. ~~Grains are 2 color mottling (light & dark yellow)  $\Rightarrow$  ox film~~



1000X, 3h sinter, 0011, POLARIZED

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# IBM Technical Notebook

## III. DENSITY WORKSHEET

STEREOPHYCNOMETER  
 TRUE POWDER DENSITY 4.95 theoretical

DENSITY - 4.87

SAMPLE I.D. 0011 DATE 10-27-88  
 SOURCE SWT OPERATOR PRD  
 TOTAL WEIGHT 19.07 g. OUTGASING CONDITIONS N<sub>2</sub>  
 TARE WEIGHT 4.06 g.  
 SAMPLE WEIGHT 14.96 g. ADDED VOLUME,  $V_A$  85.57 cc  
 CELL HOLDER VOLUME,  $V_C$  34.85 cc

OPERATIONAL EQUATION  $V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_1} \right]$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_1$  = Pressure Reading after Added  $V_A$

|         | DATA             | 3.685 | 3.691 | 3.692 |
|---------|------------------|-------|-------|-------|
| RUN 1   |                  |       |       |       |
| $P_2$   | <u>19.646</u>    |       |       |       |
| $P_1$   | <u>5.331</u>     |       |       |       |
| $V_p$   | <u>2.999</u> cc  |       |       |       |
| DENSITY | <u>4.99</u> g/cc |       |       |       |
| RUN 2   |                  |       |       |       |
| $P_2$   | <u>19.831</u>    |       |       |       |
| $P_1$   | <u>5.372</u>     |       |       |       |
| $V_p$   | <u>3.076</u> cc  |       |       |       |
| DENSITY | <u>4.86</u> g/cc |       |       |       |
| RUN 3   |                  |       |       |       |
| $P_2$   | <u>19.683</u>    |       |       |       |
| $P_1$   | <u>5.333</u>     |       |       |       |
| $V_p$   | <u>3.07</u> cc   |       |       |       |
| DENSITY | <u>4.87</u> g/cc |       |       |       |
| RUN 4   |                  |       |       |       |
| $P_2$   | <u>19.718</u>    |       |       |       |
| $P_1$   | <u>5.341</u>     |       |       |       |
| $V_p$   |                  |       |       |       |
| DENSITY |                  |       |       |       |

## III. DENSITY WORKSHEET

STEREOPHYCNOMETER  
 TRUE POWDER DENSITY

SAMPLE I.D. 2201 DATE 10-27-88  
 SOURCE PRD OPERATOR PRD  
 TOTAL WEIGHT 18.07 g. OUTGASING CONDITIONS N<sub>2</sub>  
 TARE WEIGHT 4.06 g.  
 SAMPLE WEIGHT 10.98 g. ADDED VOLUME,  $V_A$  85.57 cc  
 CELL HOLDER VOLUME,  $V_C$  34.85 cc

OPERATIONAL EQUATION  $V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_1} \right]$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_1$  = Pressure Reading after Added  $V_A$

|         | DATA             | 3.568 | 3.566 | 3.566 |
|---------|------------------|-------|-------|-------|
| RUN 1   |                  |       |       |       |
| $P_2$   | <u>19.865</u>    |       |       |       |
| $P_1$   | <u>5.568</u>     |       |       |       |
| $V_p$   | <u>1.548</u> cc  |       |       |       |
| DENSITY | <u>7.21</u> g/cc |       |       |       |
| RUN 2   |                  |       |       |       |
| $P_2$   | <u>19.720</u>    |       |       |       |
| $P_1$   | <u>5.530</u>     |       |       |       |
| $V_p$   | <u>1.522</u> cc  |       |       |       |
| DENSITY | <u>7.21</u> g/cc |       |       |       |
| RUN 3   |                  |       |       |       |
| $P_2$   | <u>19.807</u>    |       |       |       |
| $P_1$   | <u>5.583</u>     |       |       |       |
| $V_p$   | <u>1.527</u> cc  |       |       |       |
| DENSITY | <u>7.21</u> g/cc |       |       |       |

0011 Rapid Temp Sintering Process parameters

10-31

|                     | $T_{set}$ | Sample (equal. values) |
|---------------------|-----------|------------------------|
| <del>10-11-88</del> | 962       | 986                    |
| <del>10-11-88</del> | 950       | 978                    |
|                     | 948       | 977                    |

note: preheat chamber and overshoot  
 $T_{set}$  needed w/ back-off on approach to get quick sintering temperature attainment

The above understood

Date

and

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Diffusion Pellet Calculations:

DOPSD!

123 std. pellet volume:  $3.25g / 6.36g/cc = 0.51 cc$

$\therefore 2201 = 0.51 cc \times 7.2g/cc = 3.67g \sim 3.75g$

$0011 = 0.51 cc \times 4.86g/cc = 2.48 \sim 2.50g$

In preheated RT @ 3:31

| <del>0011</del> | $T_{set}$ | $T_s$ | $T_{sample}$ |      |
|-----------------|-----------|-------|--------------|------|
|                 | 948       | 9??   | 933          | 3:31 |
|                 |           | 956   | 965          | 3:33 |
|                 | 958       | 964   | 974          | 3:35 |
|                 | 950       | 956   | 974          | 4:20 |
|                 | 951       |       |              | 4:21 |

backing off now to maintain temp. till EQ

for note

42 11-7-88

IBM Technical Notebook

Survey 2212 sintering time versus rel density

| <u>h</u>  | <u>rel D(%)</u> | <u>wt</u> |
|-----------|-----------------|-----------|
| 0         | 68.4            |           |
| ✓ (0.08)  | 65.9            | 0.97      |
| ✓ 0.25    | 61.1            |           |
| ✓ 0.5     | 59.7            |           |
| (16) (70) | 54              | ✓         |
| ✓ 120     | 51              | ✓         |

small pellet density determination probably not as accurate

14 16h (not listed in book)

post

0.88 1.15 0.216 0.22 4.0 / 6.45 62

redo

10-2-88 0011 Analytical IBM Technical Notebook

Sample 43  
normalization

| El. | wt % | theo. M % | ANA M % |
|-----|------|-----------|---------|
| Ca  | 22.4 | 0.86      | 0.875   |
| Sr  | 8.24 | 0.14      | 0.147   |
| Cu  | 40.6 | 1         | 1       |

Example calc.  
 $\frac{Ca\ wt\ \%}{Ca\ wt\ \%} = 0.639 / 0.639 = 1$   
 $\frac{Sr\ wt\ \%}{Sr\ wt\ \%} = 0.094 / 0.639 = 0.147$   
 $\frac{Cu\ wt\ \%}{Cu\ wt\ \%} = 0.539 = 0.825$

11/3  
 0011 pellet 2 for 16h diffusion sinter  
 Pre 4,000/30,000 slightly irregular

2.85 1.531 0.196 0.913 ~3.12 /4.95 = 63 — perfect  
 2.81 ~1.36 0.14 0.639  
 0.64 4.4 ↓ = 89

0201 4,000/30,000 PRE

3.78 1.365 0.194 0.723 5.23 = 72.4% (too high?)

11/4  
 0011-2 cut into 2 slices. Didn't add block thickness so unequal.  
 1 ~ 2.30 cm thick 1 ~ 0.179 cm

↓ Post will use for final press  
 875C for 30 hrs → pellet has warped, grown large voids like  
 xstals and sagged. Obviously metastable.  
 previous 3h sinter showed no evidence of instability.

11-28-88

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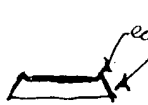
IBM Technical Notebook

44 11-9 2201 pellets  
 3200/28  
 2013 2.99 1.351 0.415 0.595 5.02 69.7 open possibly  
 2.96 ~1.306 0.392 0.498 ~5.98 ~83.3+ defects pycnometer  
 2-3 min 872C SINTER (SLO ATTAINMENT 12 MIN VERSUS 1: T<sub>SMT</sub> = T<sub>AT</sub> + 3 min) 86  
 air = 85

3300/30  
 2014 1.16 1.082 0.245 0.225 5.16 71.7 5 min.  
 1.15 1.050\* 0.210\* 0.182 6.32 87.5 double  
 86

2015 1.17 1.086 0.248 0.230 5.09 70.7 {broken before  
 sintering  
 reground & Repressed } pellet 201-11

2016 0.99 1.094 0.205 0.193 5.13 71.25 to temp 1845  
 \*† 0.98 1.06 0.185<sup>up</sup> 0.163 6.01 83.5 out 2.15  
 \* (0.178) 0.158 6.2 86 30 min

\*†: 201-4,5 some evidence of drooping  edge droop in pellet. reduce temp 5C

2700/29  
 2017 1.2 1.084 0.254 0.238(5) 5.03 69.9 to temp 2727-8  
 1.01 ~1.86 0.185 0.163 15  
 1.06 1.19 1.05 ~0.225 0.195 6.1 84.7 15



# 11-10 Sintering Summary <2201 data>

201-2

|        | temp              | SINTER | green             | POST        |                              |
|--------|-------------------|--------|-------------------|-------------|------------------------------|
| 201-8  | 872C              | 2 min  | 71.25             | 85.6        | ← 011-2201 P3 pressed pellet |
| 201-3  | 872               | 2-3    | 69.7 <sup>+</sup> | 86          | ← (large die)                |
| 201-4  | 875C <sup>+</sup> | 5      | 71.7              | 87.5        | 86.1 ave                     |
| 201-9  | 872C              | 5      | 71-               | 84.7        |                              |
| 201-7  | 872C              | 15     | 69.9              | 84.7        |                              |
| 201-6  | 875C <sup>+</sup> | 30     | 71.25             | 83.5        |                              |
| 201-10 | 872C              | 1h     | 70.4              | 86.7 → 85   |                              |
| 201-1  | 875 <sup>+</sup>  | 2h     |                   | 84-         |                              |
| 201-2  | 875               | 30h    |                   | (76.1) → 79 |                              |

not bearing  
 2/2/72  
 87

Record keeping: 201-2 30h 875C ~ 75% (pyc): irregular pellet growth  
 resulting in varying local densities  
 201-3 0.608 dia. pellet for pressure diffusion sinter  
 201-5 regd → 201-11

11-11 Gas pycnometry gives an averaged rel density for pellets 1, 7, 8, 9  
 (wght 4.6g) of 86.75g vs 84.75 (reasonable agreement), mostly  
 closed porosity.

46-14 SINTER 870-875C IBM Technical Notebook

201-8 perfect pellet ~3000/29000 [ALL SINTER TIMES ARE 1mw attainment + 1mw EQ SOAK + Δ SINTER time]

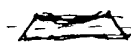
|       |      |       |       |       |      |       |       |
|-------|------|-------|-------|-------|------|-------|-------|
| POST  | 1.19 | 1.081 | 0.253 | 0.232 | 5.13 | 71.25 | green |
| 2 MIN | 1.17 | 1.038 | 0.225 | 0.190 | 6.16 | 85.6  |       |

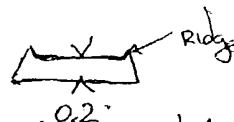
|       |           |       |       |       |      |       |       |
|-------|-----------|-------|-------|-------|------|-------|-------|
| POST  | 201-9 1.2 | 1.075 | 0.259 | 0.235 | 5.11 | 71.00 | green |
| 5 MIN | 1.09      | 1.036 | 0.231 | 0.195 | 6.10 | 84.7  |       |

|      |             |                              |       |          |      |                              |           |
|------|-------------|------------------------------|-------|----------|------|------------------------------|-----------|
| POST | 201-10 1.10 | 1.083                        | 0.236 | 0.217    | 5.07 | 70.4                         |           |
| 1h   | 1.09        | <sup>1.043-1.07</sup> 1.057* | ~0.2† | 0.175(5) | 6.21 | <del>86.25</del> (accurate?) | see below |

201-11 Pellet was regd & repressed from broken pellet. Also, die RAM force resulting in much high uniaxial pressure (of true edge) 12,000

|       |       |       |      |       |
|-------|-------|-------|------|-------|
| 1.169 | 0.252 | 0.222 | 5.04 | 70.00 |
|-------|-------|-------|------|-------|

\* linear average dia due to slumping. (- )  
 † w pellet interior after edge ridge worn away



? probably slightly less due to exclusion of ridge volume and linear average approx after flattening; 15 μm

|        |       |       |       |       |      |    |                        |
|--------|-------|-------|-------|-------|------|----|------------------------|
| 201-10 | 0.90† | 1.057 | 0.168 | 0.147 | 6.12 | 85 | better (more accurate) |
|--------|-------|-------|-------|-------|------|----|------------------------|

11 2.96 (298)

|        |       |       |       |      |     |        |
|--------|-------|-------|-------|------|-----|--------|
| 201-11 | 1.357 | 0.412 | 0.596 | 4.97 | 5.0 | (69.4) |
|--------|-------|-------|-------|------|-----|--------|

|       |        |       |       |      |      |
|-------|--------|-------|-------|------|------|
| 2.935 | ~1.315 | 0.365 | 0.496 | 5.94 | 82.5 |
| 2.945 |        |       |       |      |      |

11-<sup>17</sup>~~12~~

201-11 cut "what" larger flattened and polished.

0011-2201 sandwich ~0.353-0.363 thick.

> From furnace top to bottom of "weight plate"  $1\frac{9}{32}"$  @ 462C  
assuming ~6 lbs for RAM & plate & x-sectional pellet area  
of  $0.212 \text{ in}^2$  load  $\Rightarrow$  28 psi

Diffusion sintering set @ 860C for ~12 hrs.

Rel density from measurement of 201-11 ~83%. On inspection  
of internal polished surface numerous burnout-like occlusions present.  
Some degree of open porosity, also.

Pyc. rel. den = 88. % thus  $\Delta$  attributable to open porosity.

0011 rel density from measure ~89%. No pyc reading done  
16h sinter @ 975C.

4:30 pm T @ 859C assume start of diffusion sintering

Plate height  $1\frac{3}{8}"$  ( $\frac{3}{32}"$  expansion due to TCE from 462C)  
(No RT measure made, but not significant)

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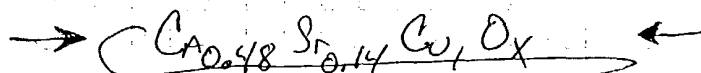
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11-28-88 <INSERT>

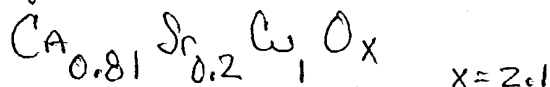
Results (by microprobe) of  $\text{CaSrCuO}_x$  melt xstals

Melt composition was from pgs. 27-29

Composition was not  $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_1\text{O}_x$  in melt, but rather



from which xstals grew of  $\text{CaSrCuO}_x$  with stoir.



Atomic wght fractions were:

|    |                       |
|----|-----------------------|
| Ca | 0.195                 |
| Sr | 0.05                  |
| Cu | 0.242                 |
| O  | 0.513 (by difference) |

Melt temp. was 1000C for 16h with cooling virtually, but NOT TOTALLY A QUENCH: UNCONTROLLED RATE REGULATED BY Puente thermal mass

11-22

IBM Technical Notebook

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Balance Bi Packs for Run

2212 - <sup>~g</sup>30.5

2201 - 12.5

0011 - 33.5

2<sup>nd</sup> Diffusion Run 2hr RAMP to 866C @ 100C plate space =  $1\frac{7}{32}$

0011 disc started @ 0.18 cm (not measured when finished, pretty was 2201 or sandwich, will try to approx)

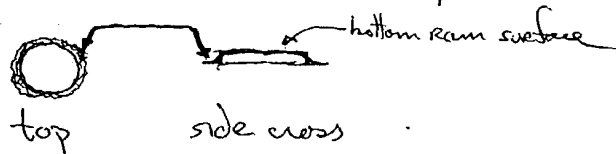
2201 ~ same 0.18

loose ~  $0.23 - 0.2 \times 0.03/\text{slice}$   $\therefore 0.18 \rightarrow 0.15$   $0.17 \rightarrow 0.14$   
so sandwich might be ~ 0.29 cm (80% of run #1)

Approx thickness by height of plate differences @ 866C  $1\frac{12}{32} - 1\frac{7}{32}$

$\frac{5}{32} = 0.23$  cm  $\therefore 0.29 - 0.23 = 0.06$  too small  $\rightarrow$  871C peak

RESULTS: "Bi" pellet has spread, apparently melting. Total thickness 0.18 cm.  
Lia generated crystalline (?) skirt around pellet periphery.



$0.18 \text{ cm} = 0.07$  " slice ~ square  $0.07 + 0.015 = 0.085$

50

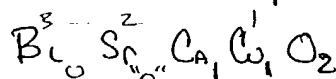
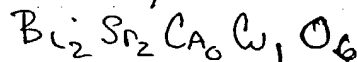
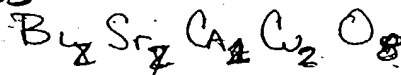
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0011-2201 Mix Calculations

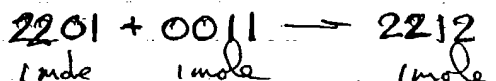
at%      at%  
 0011      2201

\*✓ +2

\*✓ +5



From "ideal" state.



|    | A.W.    | 0011  | 2201    | 2212     |
|----|---------|-------|---------|----------|
| B  | 208.98  | -     | 417.96  | 417.96   |
| Sr | 87.62   | -     | 175.24  | 175.24   |
| Ca | 40.08   | 40.08 | -       | 40.08    |
| Cu | 63.54   | 63.54 | 63.54   | 127.08   |
| O  | 15.9994 |       | 95.9964 | 127.9952 |

$135.6188 + 752.7341 = 888.3552$

|    |                |                     |                        |
|----|----------------|---------------------|------------------------|
| B  | $0(0.4)(0.8)1$ | $(2.15)(1.6)(0)(1)$ | $(2.15)(1.6)(1.17)(2)$ |
|    | -              | 449.307             | 449.307                |
| Sr | 12.2668        | 140.192             | 147.2016               |
| Ca | 34.4688        | -                   | 40.3284%               |
| Cu | 63.54          | 63.54               | 127.08                 |
| O  | 31.9988        | $\sim 95.9964^*$    | $\sim 127.9952$        |

142.2744

749.0354

891.912296 / (891.3098)

% dev

+8.6%

\*(5.825)15.9994  
 93.19651

99.6% (2.15 etc)

99.92%

The above understood and witnessed by

Date

and

Date

CONTINUATION...

1 mole "0011" + 1 mole 2201  $\Rightarrow$  011 + 529 wt % 2201

142.2744g  $\downarrow$  752.7364g

$$142.2744g + (0.02)(142.2744) = 145.12g$$

$$2.84549$$

$$9.485 \quad 9.49 \quad 0.19 \quad = \quad 9.675 \quad \left. \begin{array}{l} 2 \text{ wt \%} \\ \text{batch size} \end{array} \right\}$$

$$142.2744g + (0.05)(142.2744) = 149.38812g$$

$$7.11372$$

$$9.485 \quad \sim 0.475 \quad = \quad 9.96 \quad \left. \begin{array}{l} 5 \text{ wt \%} \\ \text{batch size} \end{array} \right\}$$

$$0.48$$

For Stoic (molar) mix =  $1.423g + 7.53g = 8.95g$  batch size

|             |        |       |  |
|-------------|--------|-------|--|
| Total Usage | 0011   | 2201  |  |
|             | 20.393 | 8.192 |  |
| %           | 61     | 66    |  |

|       |       |        |                |             |
|-------|-------|--------|----------------|-------------|
|       | cc    | cc     | vol %          | wt %        |
| roll  | 2.37  | 0.0264 | 1.0%           | 2.          |
| table | 2.37  | 0.0736 | 3              | 5           |
|       | 0.356 | 1.045  | <del>25%</del> | <u>stoc</u> |

|        |                |      |      |                |
|--------|----------------|------|------|----------------|
| STOIC: | B <sub>2</sub> | Sr   | Ca   | C <sub>2</sub> |
| "2201" | 2.15           | 1.6  | 0    | 1              |
| "0011" | 0              | 0.14 | 0.86 | 1              |

2.15 1.74 0.86 2 versus poly 2.15 1.68 1.12 2

The above understood and witnessed by

Date

and hv

Date

52 Stoic Mixing

IBM Technical Notebook

0011 - 2201

~1.43 g ~7.53

MIX STARTING @ 3:00 P.M., 50mls isopryl.  
5cc  $ZrO_2$  balls  
2/3 full

NOTE: From bottom pg 51 can be seen this Additive approach will yield a theoretical molar comp { 0.1 M larger in Sr  
0.34 M less in Ca

i.e. ~~Strontia rich~~, Calcium poor

8.96 g added initially, 8.85 g recovered's 1.2% loss (98.8 yield)

Stoic 1 Pre 2700/27,500

3.11 1.36 0.486 0.706 4.41 ~68.9

$0.25(4) + 0.75(7.2) = 6.4$  vol% basis, ~ density calc

Rxn. (SINTER) temp to be 852C

Pellet melted indicating lower mp liq  $\phi$  exists in system & later xstallized. Predominantly 1 lath-like  $\phi$  w/ exaggerated growth as in 2201 120h sample.



12-5

4:20 P.M. // 4:25 @ temp

0011-3 placed in preheated rapid temp set @ 951C ( $T_{\text{imp}} = 975C$ )  
 for overnight sintering

No pre data on density due to irregular shape caused by pellet crumbling during isopressing.  
 unipress  $\rightarrow 6000, 150 - 29,000$  PSI wght  $\sim 3.1g$  <sup>3.0-2.9</sup>

12/6

4:30 Slow cooling begun  $\therefore \Delta T_{\text{sinter}} = 17h @ 875C$

Post 2.86g  $\sim 0.460$  mm thick radius might have been  $\sim 1.38$

estimated density  $0.666cc @ 3.1g \sim 4.68 / 5.00 \approx 93$  (may be high)  
 $3.0 \quad 4.5 / \downarrow \quad 90$  better

0011-3

0.181" thick

Slice 1  $\rightarrow 0.09$ " after cleaning // post polish  $\rightarrow$  N/R

Slice 2  $\rightarrow 0.074$   
 $0.179$  ✓

2201-8  $1.038$  dia  $\therefore$  area  $= \pi D^2 / 4 = 0.85cc^2$   
 $0.409 \quad = 0.525 in^2 \quad 5.75 lbs / .525 in^2 \sim 11 psi$

2201-8 (top)



Pellet configuration @ START  $\sim 3:55$  p.m. thickness -  $0.34mm$

0011-3

Ramp  $\rightarrow 434$  Set point -  $800C$  Dwell -  $12h$   $1\frac{1}{2} @ 380C$

12/7 Result: no melting, pellets bonded w/ little deformation.

12/8 After 24h  $825C$  Anneal no evidence of liq., but bond breaks after handling at pellet interface with some "rxn etching" of 0011 pellet surface leaving thin, <sup>even</sup> layer of 2201 (or rxn prod) behind.

54  
12-6

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~~1st 2201~~ SECOND 2201 Synthesis  $\text{Bi}_{2.15}\text{Sr}_{1.6}\text{Cu}_1\text{O}_8$

$\text{Bi as Bi}_2\text{O}_3: 30.0543 \times 2 = 60.1086 \text{ } 60.11$

$\text{Sr @ SrCO}_3: 14.1724 \quad 28.3448 \quad 28.35$

$\text{Cu @ CuO}: \frac{4.7724}{48.9991 \text{ g}} \quad \frac{9.5448}{97.9982 \text{ g}} \quad 9.54$

$\sim 0.7019 \text{ conversion factor for } \text{CO}_3 \rightarrow \text{O} \quad 28.3448 (0.7019) = 19.898$

Estimate  $\sim 89 \text{ g}$  "batch recovery"  $\frac{97.9982 - 8.4468}{89.55} \text{ CO}_2 \text{ loss}$

12-7

$\text{tare } 202.54$   
 $\text{Bi}_2\text{O}_3 \quad 262.68$   
 $\frac{262.68}{60.13} - 60.11 = +0.02 \checkmark$

$\text{tare } 262.68$   
 $\text{SrCO}_3 \quad 291.03 \leftarrow 291.28.35 \text{ wgt } 28.36 \text{ tared } 28.36$   
 $\frac{291.03}{28.35} \Delta \checkmark$

$\text{CuO } 300.57 \quad (300.57/9.54) \text{ wgt } 9.55$   
 $\frac{300.57}{291.03}$   
 $\frac{291.03}{9.54} \Delta \checkmark$

12-8

97.92 / recovery after drying overnite  
 98.02 theoretical  $\approx 99.9\% \text{ yield } 0.1\% \text{ mixing loss}$

to pg 56  $\rightarrow$

IBM Technical Notebook

55

12-7-88

011  
9.49  
9.48  
0.02  
9.46

~~011~~

2201  
0.48  
0.50  
0.01  
0.49

theor.  
wgt  
resid  
actual = 9.95

std. 1-1.5h 5min ZnO<sub>2</sub>/Iso  
grind mix, screening & drying.

12-8-88

Recovery : 9.84 g / 9.86g theoretical = 99.8% > 0.2% loss

60.87  
cont tare 51.04/5  
9.83 transferred

0011-2201-5W(3V)-1

Post 8500/29,000

2.31 1.17 0.704 0.690 3.35 ~67%

Pellet larger than usual, 1.75g max in future might be considered.

1.183 0.715 CRACKED, measurements ~~N/A~~

12-9

5W-2 900C 8500/39,000

1.27 1.174 0.382 0.414 3.07 61.4!

3:55 in preheated furnace → 4:00 to temp @ 900C  
Post 5 MIN

1.24 1.111 0.36 0.349 3.55 71—

15 MIN NO SIGNIFICANT CHANGE

12-12 to temp ~ 10:30 A.M. (check: 10:45 → no slumping) → SWIR till 12:30  
12:15 A.M. stop-cool initiated  
~~11:45~~  
~2h

1.24 1.055 0.33 0.29 4.28 ~86%

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12-8-88 2201 SynII cont. (from p. 54)

crucible tare  $\frac{186.68}{88.79} \rightarrow 186.68 \rightarrow 192.29 \text{ w/ top}$   
 $\frac{88.79}{97.89}$

10:00 A.M.  $\rightarrow$  575C hold 1h  
 11:00  $\rightarrow$  800C  
 12-9 11:00 AM cool, required to < 100 mesh

$\frac{182.23}{88.95} \rightarrow 93.28$  (weight after sintered powder body removed)

$\frac{93.44}{88.95} \rightarrow 184.02$  if 88.79 used after grinding  
 $\frac{88.95}{92.07} \rightarrow$  to temp. (866C) @ 1:00 p.m.  
 $\Delta 1.21 \text{ in grinding } 1.3\%$   
 $97.98 - 93.28 = 4.67$   
 $97.89 - 89.55 = 8.34$  } 55% REACTED

1:00 - 5:00 pm 866C, shut down for weekend (may restart sooner)

12-12-88

to temp 866C @ 10:00 A.M.  
 off @ 7:00 A.M. 12/13/88

PARTIAL MELTING, "CLASSIC" EUTECTIC lamellar and large 2201 lathes.

Date and sign every entry.  
entry witnessed. Submit an  
anything possibly new and invent.

y possibly important  
Disclosure of

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\*Register with local Recorder

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~~12-14-88 2201 Syn III~~

~~working Jan 6000 202.75~~

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

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12-14-88

SYNTH 2201

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mixing jar tare 202.75

Be as  $Be_2O_3$  30.0543

Sr as  $SrCO_3$  14.1724

Cu as  $CuO$  4.7724

x 2

= 60.11

28.35

9.55

98.01

- 8.5  $CO_2$  loss

89.51

$Sr/Be = 0.744$

for 0.8  $Sr = 1.72$

$Be_2O_3$  262.86

tare 202.75

60.11

291.10(19)

262.85

28.35(5)

300.75

291.20

9.55

PRE CAL I

crucible + 185.84

tare 87.99

97.85

97.85/98.01 0.2% mix loss

12-20 Post 750C 16h calcination

crucible + 181.15

↓

87.98

93.17

post grav 92.70

NO RXN w/ Pt. ; lime green color/bottom, uniform throat

except for top 1/2 edges (grey)

93.17 - 97.85 = -4.68 / 8.5 = 55%  $CO_2$  lost

post gr

crucible + 180.70

↓

87.98

(92.72)

12-21-88 Post 790C 20h calcination

178.10

87.98

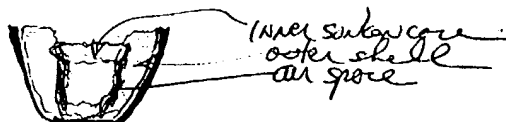
90.12

Material looks very good, smooth indicating lamellar structure

Uniformly black, sparkling sinter body; An outer shell

89% RXN close to completion # 98%

And inner core structure. (see below)



to page 60

The above understood  
 and witnessed by \_\_\_\_\_

Date

and  
 by

Date

12-14-8

# $Y_1Ba_2Cu_3O_x$ Implantation Experiment

PRE - film on  $SrTiO_3$  3500/39000  
 3.07 0.448 0.485 0.799 3.84 ~60.4 %



← line 'MARKER' || to long axis of triangular  $SrTiO_3$  implant  
 implant orientation - NOTE: MARK ON UNDERSIDE of pellet  
 ∴ film side opposite

3.02 1.271 0.396 0.508 6.02 94-95

3.05 1.448 0.476 0.784 3.89 ~61



← line 'MARKER' || to long cutting axis of two pellets (cut on line)  
 implant orientation - see NOTE above for polished side orient.  
 2.99 1.272 0.391 0.497 6.02 94-95

5

5:12 p.m. 475°C @ 10°C/min to 975 1500°C/10°C/min = 50 min ~ 6:00 p.m.  
 Cutting  $SrTiO_3$  implant: measures 0.5" on saw (0.025-0.505 tangents)  
 $\frac{1.272}{2.54} = 0.485$  ✓

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12-21-88 Cakination III 2201-B3

X-RAY SHOWS DISTINCTLY NOT SINGLE  $\phi$ , even though material looks "OK."

total 177.04  
 cur 87.98  
89.06 88.2

12-22-88

175.7 - (-1.34) slight sticking (exn) w/ cur. bottom  
87.98  
 87.72 - 89.51 (theo.) = 1.79 g greater than theoretical loss  
could be grinding loss 2%

PRE  
 850 cal

174.93 total  
87.93 tare (after acid cleaning)  
 87. — g 0.72 g grinding loss (consistent w/ previous losses)  
 + X-ray slide

POST  
 12-22-88

174.83  
87.93  
 86.90 - 150.10 100% FXN ! constant weight  
 not superconducting but not surprising  
 batch #1 wasn't either



12-27-88

Summary various RKN pellets:

5 wt% 2201 in 0011 for 16h @ 850C SEM

5 wt% 2201 in 0011 for 2h @ 975C SEM

[0011-2201 ~~pressure bonded~~ <sup>stochastic mixture</sup> pellet: 13h 850C } later  
1/2" Ø formation, exaggerated grain growth/warpage]

0011 @ 975C 17h SEM STD.

2201 @ 875C 1h SEM STD.

2212 @ 853C 5min SEM STD.

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12-29-88 Dave's Compositions

| # | Y       | Ba     | Cu     | Y      | Ba     | Cu   |
|---|---------|--------|--------|--------|--------|------|
|   | (0.157) | (0.33) | (0.50) | 0.17   | 0.33   | 0.50 |
|   | 0.15    | 0.33   | 0.52   | 0.0639 | 1.9038 | 3—   |
|   | 0.17    | 0.35   | 0.48   | 1.0625 | 2.1875 | 3—   |
|   | 0.19    | 0.33   | 0.48   | 1.1875 | 2.0625 | 3—   |
|   | 0.19    | 0.31   | 0.50   | 1.14   | 1.86   | 3—   |

Calculated Compositions (calculations next page)

| #  | Y                 | Ba*                     | Cu                | total |   |
|----|-------------------|-------------------------|-------------------|-------|---|
| 1) | 1.91937<br>(1.92) | 6.51253<br>(6.51)       | 3.97697<br>(3.98) | 12.48 | ← |
| 2) | 1.69356<br>(1.69) | 6.51253<br>(6.51)       | 4.13605<br>(4.14) | 12.34 | ← |
| 3) | 1.92              | 6.90723<br>(6.91)       | 3.81789<br>(3.82) | 12.65 |   |
| 4) | 2.14578<br>(2.15) | 6.51<br>0.33            | 3.82<br>0.48      | 12.48 | ← |
| 5) | 2.15              | 6.1783<br>(6.18)<br>3.1 | 3.98              | 12.31 | ← |

\* Ba as  $BaCO_3$   
 Y as  $Y_2O_3$   
 Cu as  $CO_3$  } NOTE: no purity corrections applied yet

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1/3/89  
 Calculations for weights summarized on page 62

2)  $Y_{0.15} Ba_{0.33} W_{0.52}$

$Y = 0.15 (225.8082) / 2 = 16.9356 \text{ g } Y_2O_3$

$Ba = 0.33 (197.3494) = 65.1253 \text{ g } BaCO_3$

$W = 0.52 (79.5394) = 41.3605 \text{ g } WO_3$

3)  $Y_{0.17} Ba_{0.35} W_{0.48}$

$Y = 0.17 (225.8082) / 2 = 19.1937 \text{ g } Y_2O_3$

$Ba = 0.35 ( ) = 69.0723 \text{ g } BaCO_3$

$W = 0.48 ( ) = 38.1789 \text{ g } WO_3$

4)  $Y_{0.19} Ba_{0.33} W_{0.48}$

$Y = 21.4518 \quad Ba = 65.1253 \quad W = 38.1789$

5)  $Y_{0.19} Ba_{0.31} W_{0.50}$

$Y = 21.4518 \quad Ba = 61.1783 \quad W = 39.7697$

1)  $Y_{0.17} Ba_{0.33} W_{0.50}$

$19.1937 \quad 65.1253 \quad 39.7697$

1/8/89

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EXPERIMENTAL #1  
 1) O<sub>2</sub> SIZED

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2 → 88.5409  $\frac{1}{0.19}$  Ba<sub>0.33</sub>Co<sub>0.5</sub>

$\frac{1}{2}$  O<sub>3</sub> - 1.92

CO - 3.98(1)

BaCO<sub>3</sub> - 6.51  $\frac{3}{6.5777}$  3.843

88.53  
 tare 76.06  
 12.47

2.3125  
 0.3900 ✓

4.3712  
 0.3900

6.9665  
~~6.9785~~ 6.9685  
 0.3888

post dry 12.43

1.922

3.98(12)

6.5777 = 12.48

→ 99.6% recovery total - Δ = 0.05

1-9-89

10.95 g after 2<sup>nd</sup> 16h 950C O<sub>2</sub> calcination

$6.5777 \cdot \left( \frac{153.3394}{197.3510} \right) = 5.11 - \Delta 1.47$   
 0.777  $\frac{12.43}{1.47}$   
 12.96 ✓

1/17 Dave) post 1h grind = 1.86 μm 3000/30,000

P1 168 1.136 0.408 0.4135 4.06 63.8%

In O<sub>2</sub> @ ~3:00 p.m. 1/10/89, to temp @ 950C projected 4:30 5:00 → 9:00  
 16h

1.64 1.011 0.354 0.284 5.775 90.8 (91)

1/4/88

4) ~~82~~ fired  
O<sub>2</sub>

Y<sub>0.19</sub> Ba 0.83 Co 0.48

~~1.89~~ 6.51 ~~3.82~~  
~ 2.15

3.8217

3.865

4.2082

Y<sub>2O3</sub> -

2.5342 6.9623 4.2093

0.3865 0.384 0.3865

2.1477 6.5783 3.8218

⇒ 12.55 g

1/10/88

Second GENERATION STARTED after grinding. No evidence of  
110 formation. Powder looks good already.

10.99 g after 2<sup>nd</sup> calcination;

10.76 post grind

~~6.58~~ (.777) = 5.11 - Δ 1.47

12.55  
1.47

11.08 g expected: 10.99 ✓

Recovered

1/17

P1 Pre 2500/30,000 to temp @ ~ 5:00 p.m.

1.60 1.14 0.399 0.4073 3.93 62% ✓✓

1/18

1.58 1.055 0.365 0.319 4.95 77.8%

Green of peaks coming up in X-ray.

66

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5) Y<sub>0.19</sub> Ba<sub>0.31</sub> Cu<sub>0.50</sub>  
 (.99) Y<sub>2</sub>O<sub>3</sub> - 2.14(13)  $\xrightarrow{2.376 \text{ target}}$  BaCO<sub>3</sub> = 6.17(96) <sup>①</sup> CuO - 3.98(10) <sup>②</sup>  
 $\xrightarrow{.99} 6.2407$   $\xrightarrow{4.4686 \text{ target}}$   $\xrightarrow{9.2092 \text{ target}}$   

$$\begin{array}{r} 2.3761 \\ 0.2287 \\ \hline 2.1474 \end{array}$$
 
$$\begin{array}{r} 6.4690 \\ 0.2229 \\ \hline 6.2411 \end{array}$$
 
$$\begin{array}{r} 4.2092 \\ 0.2282 \\ \hline 3.9810 \end{array} \Rightarrow 12.3695$$
  
 $\sim 12.37$

12.34(3) collected after mix // 12.34/12.37  $\sim \Delta 0.24\%$  ✓

$6.2411 - 4.8493 = 1.392$

$$\begin{array}{r} 63.50 \\ 51.17 \\ \hline 12.33 \end{array}$$
 
$$\begin{array}{r} 62.20 \\ 51.17 \\ \hline 11.03 \end{array}$$
  $\Delta 1.3 / 1.39 = 93.5\%$

11.00 post GRIND

$$\begin{array}{r} 62.17 \\ 51.18 \\ \hline 10.99 \end{array}$$

post Cu II 62.11

$$\begin{array}{r} 11.63 \\ - 0.88 \\ \hline 10.75 \end{array}$$

Post grind 10.46  
 P1 3333/30,000 ~~PRE~~  
 1.60 1.440 0.244 0.40 4.00 62.9 ✓  
 Post 1.56 1.266 0.210 0.267 6.00 (94 = 91)  
 Good densification, no apparent liq, CuO islands present.

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2201

P1B3 2500/30000  
 PRE 1.94 1.09 0.391 0.365 5.315 73.8%  
 Post 15 min @ 860  
 1.94 1.06 0.355 0.313 6.2 86%

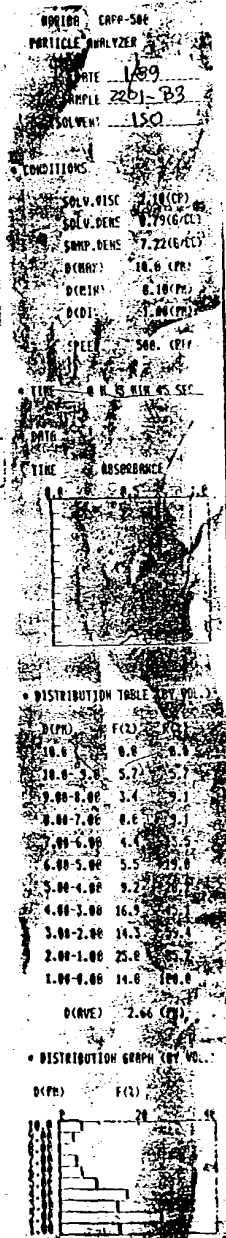
2 wt% 2201 in 0011 1/13/88

9.49  
 0.19  
 9.58 some leaking during 0.5h mix : 9.05 g  
 9.05 g  
 8.68 g final  
 0.37 g loss  
 8.68 g  
 0.37 g

2 wt% P1 4200/30,000 to temp @ ~5:00 p.m.  
 Pre 1.70 1.163 0.499 0.53 3.21 ~64.2  
 1.69 1.21 0.525 0.60 2.82 56.4  
 1.194 - 1.227  
 same slumping - Δ 12%

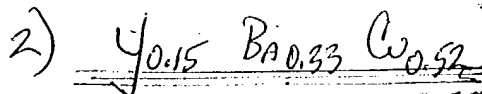
Cuts yield : 1.57 mm inside 0.30  
 1.12 mm center 0.25  
 polished → 1.79 mm outside 0.380 (tan)

+ 26.52 26.03 25.94  
 post 25.52 25.52 25.45  
 1000 → 1000 μm 490  
 510



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bottle tons: 74.55

$Y_2 O_3 - 1.6936$   ~~$CoO - 6.5125$~~   $CoO - 4.1361$   
 $BaCO_3 - 6.5783$

(.2270'5)  $\frac{1.9206}{0.22705} \sim 1.6936$   $\frac{6.8066}{0.2284(8)} - 6.5782$   $\frac{4.3651}{0.2288} - 4.1363$  total  $(0.0004) \sim 12.41$

1/17 1<sup>ST</sup> CALCINATION

66.53 (12.37 measured from mixing)  
 tare  $\frac{54.16}{12.37} \sim 12.41 = -\Delta 0.3\%$

$6.5783(.277) = 5.111 (-1.47)$   $\frac{12.37}{-1.47} \sim 10.90$  expected yield (less transfer losses)

1/18 POST  $\frac{66.53}{65.15(05)} - \Delta \frac{1.38(48)}{}$  tare 54.20 recovery  $\frac{65.05}{54.2} \sim 10.85$  total RXN.

2<sup>ND</sup> CAL (16h as above)

1/19 POST  $\frac{65.02}{54.2} \sim 10.82$   $\sim$  constant 10.79 recovery

Notes: large liq. stains (formation) during 1<sup>ST</sup>/2<sup>ND</sup> cal unlike

PRE P1 1  $\frac{1}{4}$  where liq was suppressed in 1<sup>ST</sup> cal { minor in 2<sup>ND</sup> }  
 3300/30,000 75C @ 5:16 temp @ 7:45, 16h  $\frac{11:45 A.M.}{6:44 \rightarrow 7:45}$

1.60 1.414 0.258 0.405 3.95 62.1%

1.57 1.227 0.216 0.255 6.16 96.9



Date and sign every entry. Have entry witnessed. Submit an Invention, anything possibly new and inventive.

possibly important disclosure of

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# IBM Technical Notebook

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1) O<sub>2</sub>

4) O<sub>2</sub>

2) O<sub>2</sub>

3) 1h iso

PSD's  
5) O<sub>2</sub>

HORIBA CAPH-500  
PARTICLE ANALYZER

DATE 1-10-89  
SAMPLE Yn Ba 33 6.05  
SOLVENT ISO-210

• CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CARX) 10.0 (PP)  
 D(CRIN) 0.10 (PP)  
 D(DIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA 0.7

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

| D(CPH)    | F(2) | F(2)  |
|-----------|------|-------|
| 10.0-5.0  | 0.0  | 0.0   |
| 10.0-5.0  | 1.2  | 1.2   |
| 9.00-8.00 | 2.9  | 4.1   |
| 8.00-7.00 | 0.0  | 4.1   |
| 7.00-6.00 | 0.0  | 4.1   |
| 6.00-5.00 | 0.0  | 4.1   |
| 5.00-4.00 | 5.5  | 5.6   |
| 4.00-3.00 | 19.0 | 25.5  |
| 3.00-2.00 | 16.5 | 46.8  |
| 2.00-1.00 | 20.9 | 74.5  |
| 1.00-0.00 | 25.1 | 100.0 |

D(CAVE) 1.00 (PP)

• DISTRIBUTION GRAPH (BY VOL.)

HORIBA CAPH-500  
PARTICLE ANALYZER

DATE 1-13-88  
SAMPLE Yn Ba 33 6.05  
SOLVENT ISO

• CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CARX) 10.0 (PP)  
 D(CRIN) 0.10 (PP)  
 D(DIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA 0.7

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

| D(CPH)    | F(2) | F(2)  |
|-----------|------|-------|
| 10.0-5.0  | 0.0  | 0.0   |
| 10.0-5.0  | 1.2  | 1.2   |
| 9.00-8.00 | 0.0  | 0.1   |
| 8.00-7.00 | 0.0  | 0.1   |
| 7.00-6.00 | 0.0  | 0.1   |
| 6.00-5.00 | 0.0  | 0.1   |
| 5.00-4.00 | 5.2  | 12.3  |
| 4.00-3.00 | 13.2 | 26.5  |
| 3.00-2.00 | 11.4 | 36.8  |
| 2.00-1.00 | 25.0 | 67.8  |
| 1.00-0.00 | 22.2 | 100.0 |

D(CAVE) 1.00 (PP)

• DISTRIBUTION GRAPH (BY VOL.)

HORIBA CAPH-500  
PARTICLE ANALYZER

DATE 1/20/89  
SAMPLE Yn Ba 33 6.05  
SOLVENT ISO

• CONDITIONS D-0.8

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CARX) 10.0 (PP)  
 D(CRIN) 0.10 (PP)  
 D(DIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

| D(CPH)    | F(2) | F(2)  |
|-----------|------|-------|
| 10.0-5.0  | 0.0  | 0.0   |
| 10.0-5.0  | 5.4  | 5.4   |
| 9.00-8.00 | 0.0  | 5.4   |
| 8.00-7.00 | 0.0  | 5.4   |
| 7.00-6.00 | 2.3  | 7.7   |
| 6.00-5.00 | 3.8  | 11.4  |
| 5.00-4.00 | 12.3 | 23.6  |
| 4.00-3.00 | 16.2 | 40.0  |
| 3.00-2.00 | 16.3 | 56.3  |
| 2.00-1.00 | 30.6 | 86.9  |
| 1.00-0.00 | 13.1 | 100.0 |

D(CAVE) 2.30 (PP)

• DISTRIBUTION GRAPH (BY VOL.)

HORIBA CAPH-500  
PARTICLE ANALYZER

DATE 1/27/89  
SAMPLE Yn Ba 33 6.05  
SOLVENT ISO

• CONDITIONS D-0.96

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CARX) 10.0 (PP)  
 D(CRIN) 0.10 (PP)  
 D(DIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

| D(CPH)    | F(2) | F(2)  |
|-----------|------|-------|
| 10.0-5.0  | 0.0  | 0.0   |
| 10.0-5.0  | 0.0  | 0.0   |
| 9.00-8.00 | 0.0  | 0.0   |
| 8.00-7.00 | 0.0  | 0.0   |
| 7.00-6.00 | 0.0  | 0.0   |
| 6.00-5.00 | 0.0  | 0.0   |
| 5.00-4.00 | 7.7  | 22.7  |
| 4.00-3.00 | 11.0 | 34.5  |
| 3.00-2.00 | 14.3 | 48.8  |
| 2.00-1.00 | 20.0 | 76.6  |
| 1.00-0.00 | 23.2 | 100.0 |

D(CAVE) 1.00 (PP)

• DISTRIBUTION GRAPH (BY VOL.)

HORIBA CAPH-500  
PARTICLE ANALYZER

DATE 1-24-89  
SAMPLE Yn Ba 33 6.05  
SOLVENT ISO

• CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CARX) 10.0 (PP)  
 D(CRIN) 0.10 (PP)  
 D(DIV) 1.00 (PP)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

| D(CPH)    | F(2) | F(2) |
|-----------|------|------|
| 10.0-5.0  | 0.0  | 0.0  |
| 10.0-5.0  | 0.0  | 0.0  |
| 9.00-8.00 | 0.0  | 0.0  |
| 8.00-7.00 | 0.0  | 0.0  |
| 7.00-6.00 | 0.0  | 0.0  |
| 6.00-5.00 | 0.0  | 0.0  |
| 5.00-4.00 | 0.0  | 0.0  |
| 4.00-3.00 | 0.0  | 0.0  |
| 3.00-2.00 | 0.0  | 0.0  |
| 2.00-1.00 | 0.0  | 0.0  |
| 1.00-0.00 | 0.0  | 0.0  |

D(CAVE) 0.00 (PP)

• DISTRIBUTION GRAPH (BY VOL.)

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Date

and

Date

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IBM Technical Notebook

|  |          |         |
|--|----------|---------|
| $S_{r7}L_{12}O \rightarrow S_{0.37}L_{0.63}O_{19}$ | $S_{rO}$ | $L_O$   |
|  | 38.34    | 50.1078 |
| $S_{rL}O \rightarrow S_{r0.5}L_{0.5}O_7$           | 51.8097  | 39.7697 |
| $S_{r2}L_O \rightarrow S_{r0.67}L_{0.33}O_3$       | 69.4250  | 26.248  |
| $S_{rO} = 103.6194 \rightarrow S_{rCO}_2$          | 147.63   | 142.47  |
| $L_O = 79.5394$                                    |          |         |
| 3.83 5.02  |          |         |
| 3.834 5.9198 $\rightarrow$ 8.8538                  |          |         |
| (5.18) 5.18097 3.97697 (6.98) $\rightarrow$ 9.1579 |          |         |
| (6.97) 6.9425 26.248 (2.63) $\rightarrow$ 9.5673   |          |         |
| $\downarrow$ $\downarrow$                          |          |         |
| 5.46 5.02 10.48                                    |          |         |
| 7.38 3.98 11.36                                    |          |         |
| 9.89 26.34 12.52                                   |          |         |
| $S_{rO}$ $L_O$                                     |          |         |

The above understood

Date

and

Date

1/17/89

0011-5 at % 201 @ 850C for attempted TEM prep.

slice 2 - 1.28 mm - 1280  $\mu$ m

slice 3 - 0.68 680  $\mu$ m

slice 2 prep: mounted side 1 measures  $\sim$  27.64  
1280

$$\begin{array}{r} \text{cum: } 300 \mu \\ 980/2 = 490 - 490 \\ 1340 \\ 850 \text{ target} \\ 26.30 - (33) \\ 1.34 - 1.29 \end{array}$$

$\sim$  20 8's on "soft" 15  $\mu$ m yields  $\sim$  900 { 150 8's on 6 give 770  
720  $\mu$ m before starting second side

$$\begin{array}{r} 26.40 \text{ after mount } 29 \rightarrow 26.21 \\ 25.69 \\ \hline 0.71 \checkmark \\ 25.69 \\ \hline 520 \end{array}$$

$$\begin{array}{r} 150 \rightarrow 26.16 \\ \hline 1430 \end{array}$$

$$\begin{array}{r} 150^{6's} 26.06 \\ \hline 330 \checkmark \end{array}$$

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IBM Technical Notebook

3) O<sub>2</sub> fired

Yan Ba 0.35 Co 0.48

$\frac{1}{2}O_3: 1.9213$

$BaCO_3: 6.9770$

$CO: 3.8217$

$\frac{2.1495}{0.2289} = 1.9212$

$\frac{7.2050}{0.2277} = 6.9773$

$\frac{4.0498}{0.2281} = 3.8218$

Some bumping, but very good mix so should be fine. 12.35 post mix

12.72 expected REDO (Bumping too critical)

$\frac{1}{2}O_3: 1.9213$

$BaCO_3: 6.9770$

$CO: 3.8217$

$\frac{2.1425}{0.2240} = 1.9219$

$\frac{7.1973}{0.2200} = 6.9973$

$\frac{4.0428}{0.2210} = 3.8218$   
 total 12.72

Mix recovery after overnight drying: 12.63/12.72 -  $\Delta 0.7\%$  (acceptable)

~ 63.82  
 loss 51.19

Post 62.38  
 51.20  
 11.19

Cal #I: 3:57 1900 w 5:15 est temp attainment  
 4:25 486C ~ ✓ seems correct

(11.17 expected)  
 Post cal II

Post grav I: 11.21  $\rightarrow$  11.14 62.35

$\frac{62.24}{51.20} = 11.05$

Very little lig formation compared to #2. Apparently need excess Ba and Co for larger lig.

0.2 g loss due to Si capstan from tube (pre-weigh) 10.8

1/27

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10.97 collected: white top layer on powder. Dry. Flake-cake very agglomerated/brittle and does not easily push out when brushed. Had to dry grind in order to produce decent powder.

10.25 recovered after dry grind

P1 3500/29000

1.62 1.425 0.266 0.424 3.82 60—%

1.52 1.321 0.245 0.336 4.52 71 %

Pre-grind & Post-grind x-rays show change of some peaks in two x-rays, however sintering calcination of pellet may return x-ray products to original  $\phi$ 's. Will do x-ray of pellet

also.  
Post: some slumping.

74. 2/16/87 123 Variation Study IBM Technical Notebook Property Pellets

#1 P2 3000/50,000 ave = 62.5  
 1.04 1.138 0.256 0.260 4 62.3  
 1.01 1.046 .22 0.187 5.34 84

#2 P2 1  
 1.02 1.123 0.264 0.261(s) 9.90 67.3  
 1.00 9.87 .223 0.168(G) 5.75 93.6

#5 P2 ✓  
 1.04 1.154 0.248 0.258 4.03 63.4  
 1.024 1.024 .224 0.184 5.54 87

Pellets in furnace @ ~10:30 A.M. 2/17/87 10°/min (pre-warmed)

T<sub>c</sub> T<sub>s</sub>  
 10:30 259 239 (?)  
 10:45 442 518 +Δ75.75  
 11:50 900.37 944

from early results ΔT<sub>BC</sub> we went down by 25. So estimated time to reach at point would be 45 mins. or 11:30 @ +Δ50 overshoot or 95°C then relaxation over ensuring 20 mins of 6°C. Relax in pellet run approximately time was 13°C. so probably close.

1:45 pm 2/17/87 in furnace @ 600C project out 2 hrs. 1:45 Mon

see page A15

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possibly important disclosure of

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2/6/89

# IBM Technical Notebook

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Experiments to look at.

Carbonate in 123

Clean gas with Ascarite

Sample 1 dense closed

porosity,  $P \approx 91\%$

cut sections from center

Sample 2 open porosity

$P \approx 87\%$

center section

thin slices or aggregate

(2) 3 pellets of each (Peter)  
 center sections of each

(1) TEM / EELS (P. Batson)

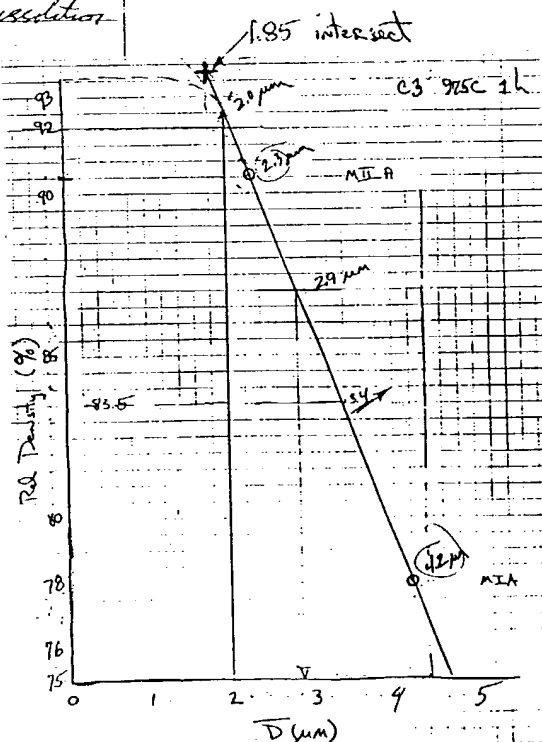
(2) Magnetometer (T. McGuire)

(3) Induction (Diane Jones)

(4)  $CO_2$  evolution on dissolution

(5) X-ray lattice

(6) XPS



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Date

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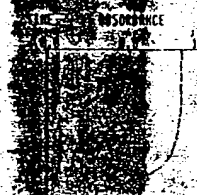
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PRIMA 100-500  
PARTICLE ANALYZER  
DATE 12/7/99  
SAMPLE C3-PA SL  
EVENT 150  
CONDIT IONS  
SOLV. VISC. 10 (CP)  
SOLV. VISC. 79 (CP)  
TEMP. DEN. 36.6 (CC)  
D (MAX) 0 (PM)  
D (RT) 10 (PM)  
D (PT) 00 (PM)  
SPEED 22000. (RPM)

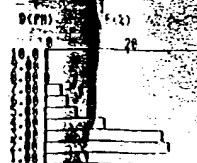
**0716Z JUL 84**

0.8



| R(1)        | R(2) |
|-------------|------|
| 0.0-0.9     | 0.0  |
| 1.0-1.9     | 0.1  |
| 2.0-2.9     | 0.2  |
| 3.0-3.9     | 0.3  |
| 4.0-4.9     | 0.4  |
| 5.0-5.9     | 0.5  |
| 6.0-6.9     | 0.6  |
| 7.0-7.9     | 0.7  |
| 8.0-8.9     | 0.8  |
| 9.0-9.9     | 0.9  |
| 10.0-10.9   | 1.0  |
| 11.0-11.9   | 1.1  |
| 12.0-12.9   | 1.2  |
| 13.0-13.9   | 1.3  |
| 14.0-14.9   | 1.4  |
| 15.0-15.9   | 1.5  |
| 16.0-16.9   | 1.6  |
| 17.0-17.9   | 1.7  |
| 18.0-18.9   | 1.8  |
| 19.0-19.9   | 1.9  |
| 20.0-20.9   | 2.0  |
| 21.0-21.9   | 2.1  |
| 22.0-22.9   | 2.2  |
| 23.0-23.9   | 2.3  |
| 24.0-24.9   | 2.4  |
| 25.0-25.9   | 2.5  |
| 26.0-26.9   | 2.6  |
| 27.0-27.9   | 2.7  |
| 28.0-28.9   | 2.8  |
| 29.0-29.9   | 2.9  |
| 30.0-30.9   | 3.0  |
| 31.0-31.9   | 3.1  |
| 32.0-32.9   | 3.2  |
| 33.0-33.9   | 3.3  |
| 34.0-34.9   | 3.4  |
| 35.0-35.9   | 3.5  |
| 36.0-36.9   | 3.6  |
| 37.0-37.9   | 3.7  |
| 38.0-38.9   | 3.8  |
| 39.0-39.9   | 3.9  |
| 40.0-40.9   | 4.0  |
| 41.0-41.9   | 4.1  |
| 42.0-42.9   | 4.2  |
| 43.0-43.9   | 4.3  |
| 44.0-44.9   | 4.4  |
| 45.0-45.9   | 4.5  |
| 46.0-46.9   | 4.6  |
| 47.0-47.9   | 4.7  |
| 48.0-48.9   | 4.8  |
| 49.0-49.9   | 4.9  |
| 50.0-50.9   | 5.0  |
| 51.0-51.9   | 5.1  |
| 52.0-52.9   | 5.2  |
| 53.0-53.9   | 5.3  |
| 54.0-54.9   | 5.4  |
| 55.0-55.9   | 5.5  |
| 56.0-56.9   | 5.6  |
| 57.0-57.9   | 5.7  |
| 58.0-58.9   | 5.8  |
| 59.0-59.9   | 5.9  |
| 60.0-60.9   | 6.0  |
| 61.0-61.9   | 6.1  |
| 62.0-62.9   | 6.2  |
| 63.0-63.9   | 6.3  |
| 64.0-64.9   | 6.4  |
| 65.0-65.9   | 6.5  |
| 66.0-66.9   | 6.6  |
| 67.0-67.9   | 6.7  |
| 68.0-68.9   | 6.8  |
| 69.0-69.9   | 6.9  |
| 70.0-70.9   | 7.0  |
| 71.0-71.9   | 7.1  |
| 72.0-72.9   | 7.2  |
| 73.0-73.9   | 7.3  |
| 74.0-74.9   | 7.4  |
| 75.0-75.9   | 7.5  |
| 76.0-76.9   | 7.6  |
| 77.0-77.9   | 7.7  |
| 78.0-78.9   | 7.8  |
| 79.0-79.9   | 7.9  |
| 80.0-80.9   | 8.0  |
| 81.0-81.9   | 8.1  |
| 82.0-82.9   | 8.2  |
| 83.0-83.9   | 8.3  |
| 84.0-84.9   | 8.4  |
| 85.0-85.9   | 8.5  |
| 86.0-86.9   | 8.6  |
| 87.0-87.9   | 8.7  |
| 88.0-88.9   | 8.8  |
| 89.0-89.9   | 8.9  |
| 90.0-90.9   | 9.0  |
| 91.0-91.9   | 9.1  |
| 92.0-92.9   | 9.2  |
| 93.0-93.9   | 9.3  |
| 94.0-94.9   | 9.4  |
| 95.0-95.9   | 9.5  |
| 96.0-96.9   | 9.6  |
| 97.0-97.9   | 9.7  |
| 98.0-98.9   | 9.8  |
| 99.0-99.9   | 9.9  |
| 100.0-100.9 | 10.0 |

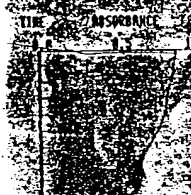
• DISTRIBUTION GRAPH (BY VOTE)



|                   |             |
|-------------------|-------------|
| WORLDWIDE         | DATE        |
| PARTICLE ANALYZER | 7/89        |
| SAMPLE            | PS          |
| SOLVENT           | iso         |
| CONDITIONS        |             |
| SOLV. VISC.       | 2.10 (CP)   |
| SOLV. DEN.        | 0.79 (G/ML) |
| SOLV. DEN.        | 0.36 (G/ML) |
| WINDKIN           | 0.0 (PH)    |
| WINDKIN           | 0.10 (PH)   |
| WINDKIN           | 1.00 (PH)   |
| SPEED             | 500. (RPM)  |

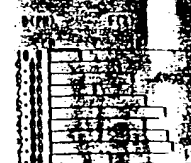
• TIME: 20 SEC

• MTR ~ 0.8



| • DISTRIBUTION |       | BY    |
|----------------|-------|-------|
| (CPI)          |       | (CPI) |
| 0.00 - 0.99    | 3.6   |       |
| 1.00 - 1.99    | 12.1  |       |
| 2.00 - 2.99    | 22.7  |       |
| 3.00 - 3.99    | 27.5  |       |
| 4.00 - 4.99    | 34.1  |       |
| 5.00 - 5.99    | 52.8  |       |
| 6.00 - 6.99    | 64.1  |       |
| 7.00 - 7.99    | 78.2  |       |
| 8.00 - 8.99    | 92.3  |       |
| 9.00 - 9.99    | 100.0 |       |
| (AVE)          |       | (CPI) |

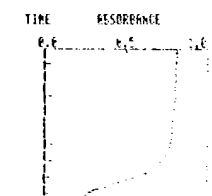
**DISTRIBUTION:** (BY MAIL)



MON. REF. CAPA. SEC.  
 PARTICLE ANALYZER  
 DATE 3/8/89  
 SAMPLE C3 Sb  
 SOLVENT ISO  
 CONDITIONS MILA  
 SOL. VISC. 2.18 CP  
 SOL. DENS. 6.79 G/CC  
 SAMP. DENS. 6.36 G/CC  
 DIAM. 18.6  $\mu$ m  
 INTRINS. 6.16 D<sub>L</sub>/G  
 DCEIV. 1.00 D<sub>L</sub>/G  
 SPEEDS 500. (RPM)

\* TIME 00 4 MIN 20 SEC

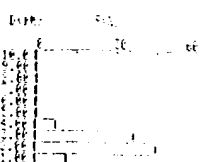
• DATA 0.8



• DISTRIBUTION TABLE (BY VOL.)

| P (P <sub>ij</sub> ) | 1   | 2   | 3   |
|----------------------|-----|-----|-----|
| 10.0 - 15.0          | 0.0 | 0.0 | 0.0 |
| 10.0 - 5.0           | 0.0 | 0.0 | 0.0 |
| 5.00-0.00            | 0.0 | 0.0 | 0.0 |
| 0.00-7.00            | 0.0 | 0.0 | 0.0 |
| 7.00-6.00            | 0.0 | 0.0 | 0.0 |
| 6.00-5.00            | 0.0 | 0.0 | 0.0 |
| 5.00-4.00            | 0.0 | 0.0 | 0.0 |
| 4.00-3.00            | 0.0 | 0.0 | 0.0 |
| 3.00-2.00            | 0.0 | 0.0 | 0.0 |
| 2.00-1.00            | 0.0 | 0.0 | 0.0 |
| 1.00-0.00            | 0.0 | 0.0 | 0.0 |

4 DISTRIBUTION: SPARSE (15 VEG.)



MOFIE: CAGE-504  
PARTICLE ANALYZES

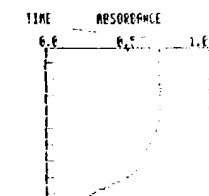
DATE 2/8/89  
CAGE C3 H6  
SAMPLE: 150

COMMENTS: MTH A

SOLV.WISC 2.18(CP)  
SOLV.DENS 6.795(GU)  
SAMP.DENS 6.3616(GU)  
D(MR): 16.8 (PP)  
D(BR): 6.3616PP  
D(DIV): 1.681PP  
SPEED 500. (PPH)

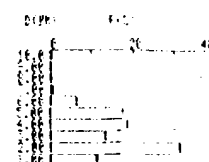
• TIME 00 4 MIN 20 SEC

• DATE 0.



| DEGREE    | F(2) | F(3)  |
|-----------|------|-------|
| 18.0-19.9 | 0.0  | 0.0   |
| 18.0-19.9 | 0.0  | 0.0   |
| 5.00-8.00 | 0.0  | 0.0   |
| 0.00-7.00 | 0.0  | 0.0   |
| 7.00-6.00 | 0.5  | 0.5   |
| 6.00-5.00 | 0.4  | 6.9   |
| 5.00-4.00 | 17.7 | 24.5  |
| 4.00-3.00 | 10.7 | 43.3  |
| 3.00-2.00 | 13.5 | 50.2  |
| 2.00-1.00 | 31.4 | 80.4  |
| 1.00-0.00 | 11.4 | 100.0 |

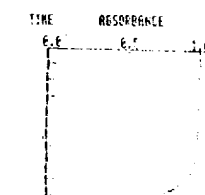
• DISTRIBUTION GRAPH (EV VOL.)



ADP:IES    CAPP:SEC  
PARTICLE NAME:VES  
DATE    2/14/88  
SAMPLE    33b: SURS  
SOLVENT?    ISO  
CONDITIONS  
SOLV. VISE    2.16(CP)  
SOLV. DENS    0.794(CP)  
CAP. DENS    0.366(CP)  
DAMP    10.0 (CP)  
DOPIN    0.18(CP)  
DOPINV    1.00(CP)  
SPEED    500 (CP)

\* TIME 6 F 4 MIN 20 SEC

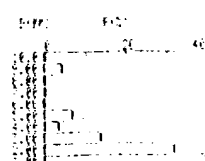
• DATE 0.93



\* DISTRIBUTION TABLE (PT VOL.)

| DATE       | F12  | F12   |
|------------|------|-------|
| 10.0 - 5.0 | 0.0  | 0.0   |
| 10.0 - 5.0 | 0.0  | 0.0   |
| 5.00-0.00  | 4.2  | 4.2   |
| 0.00-7.00  | 0.0  | 4.2   |
| 7.00-0.00  | 0.0  | 4.2   |
| 0.00-5.00  | 0.1  | 4.4   |
| 5.00-4.00  | 0.0  | 11.1  |
| 4.00-2.00  | 3.2  | 14.3  |
| 3.00-2.00  | 13.9 | 26.2  |
| 2.00-1.00  | 31.0 | 60.1  |
| 1.00-0.00  | 25.9 | 100.0 |

• DISTRIBUTION GROUP 499 46...



The above understood  
and witnessed by:

Date \_\_\_\_\_ and \_\_\_\_\_

Date: \_\_\_\_\_



IBM Technical Notebook

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2/7/89

$\rho < 87\%$  PII mill  $\bar{D} = 4.21 \mu m$  (quick)

3333/28500

Pre wght: 3.46 (of 3.5) some deformation during iso pressing, but  $\Delta$  wght minimal so no density can be deduced.

Post 975C 1h

3.41 1.402 0.448 0.69 4.94 (77.7)  $\rightarrow$  78% 4.2 too low

PII mill  $\bar{D} = 2.34 \mu m$  (slow)

PRE 3900/29,000

3.46 1.453 0.543 0.9 3.84 60.5 rh reasonable

3.40 1.285 0.456 0.59 5.76 90.6  $\langle$  NEED SLIGHTLY HIGHER  $\rangle$

Tomorrow  $\rightarrow$  will mill on

the

Yields:  $\frac{Pre}{50}$  MI :  $\frac{Post}{48g}$

gap B

gap A { 24 MIIA: 20g  
16 MIIA:  $\frac{1}{2}$

20.5

error in pre-weights

78 M4A  $\bar{D} = 1.85$  PRE - 4000/30,000 [20/mm to 675 10/mm to 975]  
 1h 975C } given

P3 (3.40) 1.452 .543 0.9 3.78 59.4  
~~3.38~~  
 3.48 1.265 0.460 0.578 6.02 94.6 vent

P4 (3.41) 1.462 .540 0.91 3.75 59. —  
 3.60 1.274 0.468 0.596 6.04 95 — heavy

P5 (3.93)<sup>+</sup> 1.457 0.561 0.955 3.67 57.7<sup>+</sup> → ≥ 58  
 3.60 1.280 0.482 0.62 5.81 91.4<sup>+</sup>  
 3.65 — 5.89 92.6 {Probably even higher}

MIFB - 4000/30,000 30 μm

P6 (3.55) 1.463 0.508 0.85 4.17 65.6  
 3.53 1.36 0.464 0.674 5.24 (82.4) vent.

P7 (3.54) 1.462 0.504 0.85 4.165 65.5  
 3.59 1.358 0.462 0.668 5.36 (84.5) heavy

P8 (3.56) 1.463 0.507 0.85 4.19 65.9  
 3.73 1.352 0.453 0.65 5.73 90.2

\* laminated on 1 side, not severe (must be 'repelletized' pellet)

6:15

IBM Technical Notebook

79

P9 4000/30000

3.57 1.462 0.517 0.87 4.1 64.5

3.56 1.354 0.463 0.666 5.35 84.0

P10 fines 4/3 as above

1.53 1.436 0.254 0.411 3.72 58.5 was expected

1.54 1.254 0.207 0.256 6.02 94.7 { doesn't look good

Pellet cutting NEXT (see pg 80 for plan overview)

Pellet 3 & 4 dedicated to vertical & horiz. slicing

Pellets 6 & 7

from tangent saw cut edge: 1 mm slices are 0.055" w/ blade

Low Density Vertical slices: 1 1.2 slices } 7 altogether + end piece  
 6 1.0 slices } and polished end (marker)

Horizontal: 2 1.0 slices mid-section  
 1 0.5 top  
 1 1.0 bottom

High Density

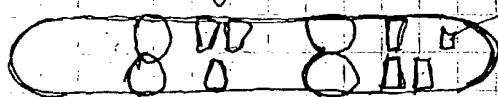
vertical: 5 slices (end lost to chipping) end polished  
 ~2mm 1 polished thick chunk  
 ~1.2mm 3 oxygenated  
 1 saved  
 horiz: 2 mid section  
 1 ea top & bottom (top chipped)

IBM Technical Notebook

2/15/89

# Oxygenation Diagram { scheme

Top View



specimens filled  
on clean  $Al_2O_3$  surface

$O_2$  flow

2/14 in and to 600C @ 20C/min; 10C/min to 800C

15min SOAK AND start RAMP to 600C @ 0.17C/min (10/h)

To 600C @ 1:30 p.m. 2/15/89 in day,  $CO_2$ -free  $O_2$ .

## Pellet (1) 0.5C

1 mm vertical slices



10/min to 850C, 10/h to 600 2dy  
(48h), quench.

- 1) 1 slice for Jerry Davis (Raman)
- 2) 1 slice for Alex for XPS of fracture surface
- 3) save remainder for future use (classified)
- 2A) 1 extra slice oxygenated

## Pellet (2) 0.5C

1 mm horizontal slices 4 up outer slices discarded

- 1) 1 slice (1.0 mm) ground to ~0.5 mm } cut 3 3mm discs w/  
ultrasonic in isopropyl Al (if possible).  
1 disc to Tom  
2 discs for TEM  
1 spare

- 2) 1 slice dedicated to P vs T to Dave's specs

## Pellet (3) 0.5C

spare for (1) x-ray lattice  
(2)  $CO_2$  evolution

2/16/89

## C4 Synthesis Preparations/Notes (ref book IV, pg 46 &amp; pg 14)

|                        | oxide<br>wt. frac.     | atomic %<br>$\frac{1}{4} \text{Ba}_2\text{C}$ | oxide<br>M.W. |
|------------------------|------------------------|---|---------------|
| $\text{Y}_2\text{O}_3$ | 0.17(5)<br>51          | .17   | 225.81        |
| $\text{BaO}$           | 0.46(5) $\leftarrow ?$ | .33   | 153.34        |

$\text{CO}$  : 0.36(25) ~ .5 79.54

Go with the new

Example Calc: wt frac deriv.

|                        |          |                                       |                              |                  |
|------------------------|----------|---------------------------------------|------------------------------|------------------|
| $\text{Y}_2\text{O}_3$ | 225.81 g | $\times \frac{17.51}{225.81} = 17.51$ | $17.51 / 109.56 = 0.159$     | oxide<br>wt frac |
| $\text{BaO}$           | 153.34 g | $\times .33 = 50.60$                  | $50.60 / 109.56 = 0.4618(5)$ |                  |
| $\text{CO}$            | 79.54 g  | $\times .5 = 39.77$                   | $39.77 / 109.56 = 0.363$     |                  |

17.51 g  $\text{Y}_2\text{O}_3$ 

1.287009

46.18 g  $\text{BaO}$   $\left\{ \frac{197.35}{153.34} \times 46.18 \right\}$  59.43 g  $\text{BaCO}_3$

|                        |  |                      |       |
|------------------------|--|----------------------|-------|
| $\text{Y}_2\text{O}_3$ | 19.19 / .99 = 19.209 $\rightarrow$ 19.21                   | $\approx \times 1.5$ | 28.82 |
| $\text{BaCO}_3$        | 50.60(2) $\left( \frac{197.35}{153.34} \right) = 65.12(5)$ |                      | 97.69 |
| $\text{CO}$            | 39.77 / .99 = 39.87  |                      | 59.72 |

$$97.69 (0.1777) = 75.91 - 97.69 =$$

$$\begin{array}{r} 186.23 \\ - 21.78 \\ \hline 164.45 \end{array}$$

A2

Administrative Notes

FINAL Batch Size For REASONABLE BULK HANDLING

$$\frac{1}{2}O_2 \quad 17.51 / .999 = 17.52(7) \approx 17.53$$

$$BaCO_3 \quad 65.12(5) / .99999 = 65.12(5) \approx 65.13 \quad \approx 343.78$$

$$CO \quad 39.77 / .999 = 39.80(9) \approx 39.81$$

$$\underline{122.47}$$

$$\begin{array}{r} 343.78(7) \quad BaCO_3 \quad \frac{1}{2}O_2 \quad 17.53^+ \text{ weighed / transferred} \\ \text{tare } 218.65 \\ \hline 65.13 \quad \checkmark \quad (AO.01?) \end{array}$$

$$\begin{array}{r} 382.36 \quad CO \quad \text{Mixing yield} \quad 122.29 \text{ g} \quad 99.85\% \\ \text{t } 343.78(7) \\ \hline 39.78 \quad (AO.03) \end{array}$$

$$\frac{122.29}{122.47} = 99.85\% \quad -AO.15$$

$$\begin{array}{r} \text{tare 1} \quad 151.42 \text{ OK} \\ \quad 82.89 \\ \quad \underline{(68.93)} \\ \quad \text{tare 2} \quad 140.48 \quad \text{bad heat dimensions} \\ \quad \quad 82.12 \\ \quad \quad \underline{58.36} = 122.29 \quad \checkmark \end{array}$$

$$\begin{array}{r} 146.97(6) \\ 88.61 \\ \underline{(58.36)} \end{array}$$

sintered much more / some l.a. form

$$\begin{array}{r} \text{tare 1} \quad 151.42 \\ \quad 144.37 \\ \quad \quad 7.05 \\ \quad \quad \underline{87.55} \end{array}$$

$$\begin{array}{r} \text{tare 2} \quad 146.97 \\ \quad 141.74 \\ \quad \quad \underline{(5.23)} \\ \quad \quad \underline{86.64} \end{array}$$

less sintered, less l.a.

$$\begin{array}{r} - 12.28 \text{ (O}_2 \text{ loss)} \\ 14.53 \text{ expected} \\ (95\% reacted) \\ 2.25 \text{ to go} \end{array}$$

$$\text{after gross } 108.71 / 110. = 98.8\% \quad -A 1.2\%$$

$$\begin{array}{r} 197.303 \quad (2) \\ \underline{88.64} \\ 108.69 \end{array}$$

|                       | <del>Y<sub>2</sub>O<sub>3</sub></del> | <del>BaCO<sub>3</sub></del> | <del>CaO</del>    | P <sup>+</sup> SLS / Result                                       |
|-----------------------|---------------------------------------|-----------------------------|-------------------|---|
| C4-1                  | 0.17                                  | 0.33                        | 0.5               | assumed stoic pure  |
|                       | 0.16                                  | 0.36                        | 0.5               | analytical determination  |
| C4-2                  | 0.17                                  | 0.33                        | 0.5               | analytical <u>lit</u>   |
| $\Delta$              | +0.01                                 | -0.03                       | —                 |   |
| C4-3                  | <del>0.16</del>                       | 0.35                        | 0.5               | analytical  |
| $\Delta$              | -0.01                                 | +0.02                       | —                 |   |
| $\Delta_{\text{net}}$ | —                                     | -0.01                       | —                 |   |
| -3E                   | 0.165                                 | 0.35                        | 0.5               |   |
| $\Delta$              | -0.005                                | +0.02                       | —                 |   |
| $\Delta_{\text{net}}$ | +0.005                                | -0.01                       | —                 |   |
| C4-4                  | 0.16                                  | 0.34                        | 0.5               | analytical  |
| $\Delta$              | —                                     | -0.01                       | —                 |   |
| $\Delta_{\text{net}}$ | —                                     | -0.02                       | —                 |   |
| C4-5                  | 0.16                                  | 0.34                        | 0.49              | analytical  |
| $\Delta$              | —                                     | —                           | -0.01             |   |
| $\Delta_{\text{net}}$ | —                                     | -0.02                       | -0.01             | Species<br>Implication $\rightarrow$ trace contam.                |
| C4-6                  | 0.16                                  | 0.34                        | 0.478             | $\text{CaO} \rightarrow \text{Ca}_2\text{O}$                      |
| $\Delta$              | —                                     | —                           | -0.02             | $\text{BaCO}_3 \rightarrow \text{Ba(OH)}_2$                       |
| $\Delta_{\text{net}}$ | —                                     | -0.02                       | -0.03             | $\text{Y}_2\text{O}_3 \rightarrow \text{Y}_2\text{O}_3 \text{ X}$ |
| C4-7                  | 0.16                                  | 0.34                        | 0.478             |   |
| $\Delta$              | —                                     | —                           | +0.008            |   |
| $\Delta_{\text{net}}$ | —                                     | -0.02                       | -0.022 $\uparrow$ |   |

C4-7 TRANSFORM TO STOIC basis

| $\text{Y}_2\text{O}_3$ | $\text{BaCO}_3$ | $\text{CuO}$     |      |
|------------------------|-----------------|------------------|------|
| 0.17                   | 0.31            | <del>0.478</del> | 0.48 |

Correct for final batch

∴  $\text{Y}_2\text{O}_3$  is good as received

$\text{BaCO}_3$  is Barium rich by 0.02 at %

$\text{CuO}$  is Copper rich by 0.02 at %



A3

Administrative Notes

Post Cal II in 60hs @ 950C in  $O_2$ 

3/27

195.52  $\rightarrow$  post 88.84 (org. rxn.)

88.64

 $106.88 - 108.69 = 1.81 / 2.25 = 80.5\%$  of remainder $\frac{12.28}{14.09} / 14.53 \text{ theor.} = 97\% + \text{loss}$ 

Maximal liq. formation.

99.57g yield (due to contamination)

{ further contamination upon re-submersion to tube for cal II reduces yield further

Peaks @ ~30.2, 29.4, 28.5  $2\theta$  Duxbury. May be  $BaCl_2$ , but could also be  $ZrO_2$ 

$$n\lambda = 2d \sin \theta \Rightarrow d = \frac{\lambda}{2 \sin \theta} \quad 100 = 3.72$$

something wrong here

$$3.72 = \frac{\lambda}{2 \sin \theta}$$

$$4.803 = \sin^2 \theta$$

4/19

From Flechaty:  $Y_{.96} Ba_{2.16} Cu_3$  ( $Y_{.32} Ba_{.72} Cu_1$ )  $O_{2.2}$ IN REFERENCE TO VARIATIONAL STUDY:  $0.16 \pm 0.01$   $0.36 \pm 0.005$   $0.5 = 1.02$

### Administrative Notes

A3

## Administrative Notes

2/17/89 page 74

975C "Property Pellets from formation study. - D<sub>2</sub>

2g pellets should give enough material for 4.4 mm thick sintered body  
allowing a slice to be cut on interior & exterior surface.

7.5 g #1 stock 1.92 used for pellet (.17 .33 .5)

7.6 g #2 stock 1.90 ↓ ↓ (.15 .33 .52)

8.5 g #3 stock ... (.17 .35 .48)

9 #4

7.7 #5 to 600C @ 20/min; 10/min to 975C 4131-625C  
3600/29,000 Quench 1h ~510

#1 P3

1.92 1.144 0.479 0.489 3.93 61.8

1.90 1.0 0.4 0.314 6.05 95-

#2 P3

1.91 1.126 0.490 0.488 3.91 61.5

1.88(?) 0.98 0.412 0.311 6.043 95-

#3 P2

1.133 0.503 0.507 3.85 60.5

1.95 0.998 0.43 0.336 5.51 86.6

-A1 1.85

#4 P2

1.139 0.481 0.490 3.88 61-

1.90 1.05 0.43 0.37 5.03 79-

1.86

#5 P3

1.145 0.46 0.474 3.99 62.7

1.87 0.993 0.388 2.300 6.2 97.5

1.86 1.05 0.41

Administrative Notes

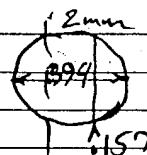
#1-5

Pellets slowing of oxygenation @ 600C for 66 hrs in O<sub>2</sub>

0.394 inches

0.157 in for center cut

0.08 = 2 mm



#1 PL1 Pre 63.5%

Pst

1.85

1.025

0.406

0.335

5.52

87

2/28

# Property Pellet Summary (to date)

|                  | scb         | lig     | X    | X    | CO   | RUN#  |
|------------------|-------------|---------|------|------|------|-------|
|                  | #1          | #2      | #3   | #4   | #5   |       |
| oxygenated       | 915 (95)    | 95 (87) | (87) | (79) | 91.5 | R3    |
| in Swenace 2/28  | 950 II (84) | (94)    | -    | -    | (87) | R2    |
|                  | 950 87      | R done  |      |      |      | R4    |
| MICRO STRUCTURES | ORIG 950    | 91 '97' | 71   | 78   | 92   | Davis |

950 II #1 & #5 pellets to temp @ 600C after 10C/min Ramp @ 6:15 pm

> oxygenation RUN

Out 10:00 A.M. 3/2 40h O<sub>2</sub>

3/27

## Administrative Notes

$$5 \text{ cc} \times \frac{6.36 \text{ g}}{\text{cc}} = 31.8 \text{ g}$$

$$\frac{\pi (2.54)^2}{4} X = 5 \text{ cc}$$

$$5.07 \text{ cm}^2 X = 5 \text{ cc}$$

$$X = 5 \text{ cc} / 5.07 \text{ cm}^2$$

$$X \approx 1 \text{ cm} \text{ or } 1/2 \text{ inch} - 1 \text{ inch with shrinkage}$$

4/24/89

#1 - Cs wt% Cu 28.7

wt% holes 36.0

Hole Concentration Conversion Formula:

Data: wt% Cu (total): 28.7

wt% holes: 36.0

$$\frac{\text{wt\% holes} - \text{wt\% Cu}_{\text{tot}}}{\text{Cu}_{\text{tot}}} = \frac{36 - 28.7}{28.7} = 0.254 \quad \text{average 'over' valence}$$

∴ add Cu valence (2) = 2.25 = average valence Cu

$$2.25 (\text{Cu}_{\text{total}}) = 2.25 (3) = 6.75 \quad \text{total Cu val}$$

$$+ 7.00 \quad \text{total Ba+Y val}$$

$$\hline 13.75$$

from sample  
4  
Y, Ba<sub>2</sub> Cu<sub>3</sub> 2.25

total charges

Take total charges & divide by two for O<sup>2-</sup>

$$13.75 / 2 = 6.88 \text{ O}_{\text{atoms}} \Rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6.88}$$

2.25

see  
page after  
next

## Notes to Kristy concerning PELLET FORMING precalculations

To estimate pellet weight for pellet pressing:

A. take dia & approx. height desired

$$1. \text{ calculate volume in cc. } (1.2 \frac{(1.22 \text{ cm})^2}{4} \times 0.35 \text{ cm} \times \pi) = 0.41 \text{ cc}$$

B. Assume some reasonable 'green' density (wt/area pressed/pellet)

0.6-0.8 (60-80%) usual for metals > 0.70 w/ small

ave. part. dias. (10.3 mm).

$$\cancel{99} (0.41 \text{ cc} / 0.8) \times \overset{\text{density theoretical}}{9.0 \text{ g/cc}} \approx 3 \text{ g of powder.}$$

I pressed @ between 16,000 & 20,000 psi.

low side for pure metal  $\therefore$

$$\frac{X}{(\text{dia})^2} = \text{desired pressure where } X = 1'' \text{ scale pressure}$$

$$X \approx 4,000 \text{ for } 0.48'' \text{ dia. dia.}$$

Administrative Notes

K. Kroll

NORIDA CAP-500

PARTICLE ANALYZER

DATE 3/14/89

SAMPLE 15061-6

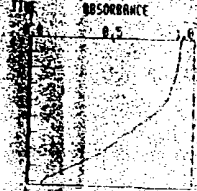
SOLVENT 150

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 2.61 (G/CC)  
D(CAN) 10.0 (PM)  
D(MIN) 0.10 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (RPM)

• TIME 0 H 15 MIN 17 SEC

• DATA 0.95

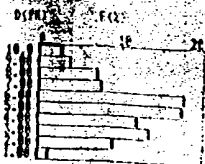


• DISTRIBUTION TABLE (BY VOL.)

| D(CPM)     | F(2) | R(2)  |
|------------|------|-------|
| 10.0 <     | 8.5  | 8.5   |
| 10.0 - 9.0 | 2.0  | 11.3  |
| 9.00-8.00  | 3.0  | 15.1  |
| 8.00-7.00  | 7.0  | 22.1  |
| 7.00-6.00  | 7.4  | 29.6  |
| 6.00-5.00  | 17.6 | 47.2  |
| 5.00-4.00  | 17.2 | 64.5  |
| 4.00-3.00  | 11.9 | 76.4  |
| 3.00-2.00  | 13.4 | 89.8  |
| 2.00-1.00  | 9.0  | 98.8  |
| 1.00-0.00  | 1.2  | 100.0 |

D(CAN) 4.04 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



NORIDA CAP-500

PARTICLE ANALYZER

DATE 3/14/89

SAMPLE CX-AL-03

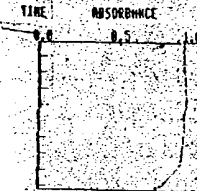
SOLVENT 150

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 3.97 (G/CC)  
D(CAN) 10.0 (PM)  
D(MIN) 0.10 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500 (RPM)

• TIME 0 H 7 MIN 36 SEC

• DATA 0.9

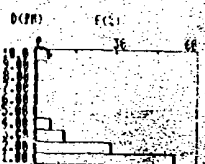


• DISTRIBUTION TABLE (BY VOL.)

| D(CPM)     | F(2) | R(2)  |
|------------|------|-------|
| 10.0 <     | 0.0  | 0.0   |
| 10.0 - 9.0 | 4.5  | 4.5   |
| 9.00-8.00  | 0.0  | 4.5   |
| 8.00-7.00  | 0.0  | 4.5   |
| 7.00-6.00  | 0.0  | 4.5   |
| 6.00-5.00  | 0.0  | 4.5   |
| 5.00-4.00  | 0.0  | 4.5   |
| 4.00-3.00  | 5.5  | 10.0  |
| 3.00-2.00  | 10.5 | 20.6  |
| 2.00-1.00  | 20.0 | 40.5  |
| 1.00-0.00  | 51.5 | 100.0 |

D(CAN) 6.57 (PM)

• DISTRIBUTION GRAPH (BY VOL.)





5/1/89  
Administrative Notes

# Analytical Results for C3 HD/LD STUDY - Holes

IBM  
RESEARCH CENTER

ANALYTICAL  
LABORATORY

IBM

## Request for Analysis

Use Ball Point Pen

|  |                              |   |
|--|------------------------------|---|
| REQUESTOR <u>T. S. Pickett</u>                                   | PROJECT NO.                  | REQUEST NO.                             |
| DEPARTMENT   | LOCATION                     | ROOM <u>2-5-225</u> PHONE               |
| REQUESTOR'S SAMPLE IDENTIFICATION <u>HD ex, LD ex</u>            |                              |   |
| APPROXIMATE COMPOSITION AND HISTORY OF SAMPLE <u>YBaCu oxide</u> |                              |   |
| ANALYSES REQUESTED   |                              |   |
| ANALYSIS METHOD  |                              |   |
| <u>low</u>   |                              |   |
| ANALYTICAL RESULTS   |                              |   |
|  | HD                           | LD                                      |
| wt% "Holes"  | 33.5                         | 34.2                                    |
| wt% Cu   | (23.5)                       | 27.0                                    |
|  | 2.21                         | 2.26                                    |
|  | 6.81                         | 4.689                                   |
| <u>tot H = %</u>   |                              |   |
| <u>4 cu</u>  |                              |   |
| Aster Reox: HD ex  | 28.7                         | wt% Cu ← 28.6                           |
| note @ 500C  | 36                           | holes                                   |
| DATE SUBMITTED <u>3/20/89</u>                                    | DATE REPORTED <u>3/24/89</u> | NOTEBOOK REFERENCE <u>4/1/89 p. 121</u> |
| ANALYST <u>T. S. Pickett</u>                                     | APPROVAL                     |   |

Nº

## Notes to Kristy concerning PELLET FORMING precalculations

To estimate pellet weight for pellet pressing:

A. take dia & approx. height desired

1. calculate volume in cc.  $(1.2 \frac{(1.22 \text{ cm})^2}{4} \times 0.35 \text{ cm} \times \pi) = 0.41 \text{ cc}$

B. Assume some reasonable 'green' density (unfired pressed pellet)

0.6-0.8 (60-80%) usual for metals > 0.70 w/ small

ave. part. dias. (i.e. 3 mm).

$$\cancel{cc} (0.41 \text{ cc} / 0.8) \times \overset{\text{density theoretical}}{9.0 \frac{\text{g}}{\text{cc}}} = 3 \text{ g of powder.}$$

I pressed @ between 16,000 & 20,000 psi.

low side for pure metal  $\therefore$

$$\frac{X}{(\text{dia in})^2} = \text{desired pressure where } X = 1'' \text{ scale pressure}$$

$$X \approx 4,000 \text{ for } 0.48'' \text{ dia. die.}$$

4/24/89

#1-C3 wt% Cu 28.7

wt% holes 36.0

Hole Concentration Conversion Formula:

Data: wt% Cu (total): 28.7

wt% holes: 36.0

$$\frac{\text{wt\% holes} - \text{wt\% Cu}_{\text{tot}}}{\text{Cu}_{\text{tot}}} = \frac{36 - 28.7}{28.7} = 0.254$$

average 'over'  
valence

∴ add Cu valence (2) = 2.25 = average valence Cu

$$2.25 (\text{Cu}_{\text{total}}) = 2.25 (3) = 6.75 \text{ total Cu val}$$

↑  
from sample  
2.25

$$+ 7.00 \text{ total Ba+Y val}$$


---

13.75

⑦

total charges

Take total charges & divide by two for  $O^{2-}$ 

$$13.75/2 = 6.88 \text{ ATOMS} \Rightarrow YBa_2Cu_3O_{6.88}$$

2.25

see  
page after  
next

## Notes to Kristy concerning PELLET FORMING precalculations

To estimate pellet weight for pellet pressing:

A. take dia & approx. height desired

1. calculate volume in cc.  $(1.2 \frac{(1.22 \text{ cm})^2}{4} \times 0.35 \text{ cm} \times \pi) = 0.41 \text{ cc}$

B. Assume some reasonable 'green' density (unfired pressed pellet)

0.6-0.8 (60-80%) usual. for metals > 0.70 w/ small

ave. part. dias. (ie. 3mm).

$\cancel{50} (0.41 \text{ cc} / 0.8) \times 9.0 \frac{\text{g}}{\text{cc}} \approx 3 \text{ g of powder}$  ← density theoretical

I pressed @ between 16,000 & 29,000 psi.

low side for pure metal  $\therefore$

$\frac{X}{(\text{dia})^2} = \text{desired pressure}$  where  $X = 1'' \text{ scale pressure}$

$X \approx 4,000 \text{ for } 0.48'' \text{ dia. die.}$

Administrative Notes

11

K. Kroll

NORION CAPA-500

PARTICLE ANALYZER

DATE 3/1/89

SAMPLE 2056-6

SOLVENT ISO

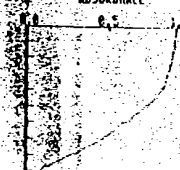
• CONDITIONS

SOLV. VISC 2.10(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 2.61(G/CC)  
D(CAN) 10.0 (PH)  
D(CIN) 6.10(PH)  
D(CIV) 1.00(PH)  
SPEED 500. (RPM)

• TIME 6 H 13 MIN 12 SEC

• DATA 0.95

TIME ABSORBANCE



• DISTRIBUTION TABLE (BY VOL.)

| D(PH)       | F(%) | P(%)  |
|-------------|------|-------|
| 10.0 -      | 0.5  | 0.5   |
| 10.0 - 9.0  | 2.8  | 11.3  |
| 9.00 - 8.00 | 3.0  | 15.1  |
| 8.00 - 7.00 | 7.6  | 22.1  |
| 7.00 - 6.00 | 7.4  | 29.6  |
| 6.00 - 5.00 | 17.6 | 47.2  |
| 5.00 - 4.00 | 17.3 | 64.5  |
| 4.00 - 3.00 | 11.9 | 76.4  |
| 3.00 - 2.00 | 13.4 | 89.8  |
| 2.00 - 1.00 | 5.6  | 95.4  |
| 1.00 - 0.00 | 1.2  | 100.0 |

D(AVE) 4.04 (PH)

• DISTRIBUTION GRAPH (BY VOL.)

D(PH) F(%)



NORION CAPA-500

PARTICLE ANALYZER

DATE 3/14/89

SAMPLE 2056-6

SOLVENT ISO

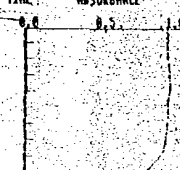
• CONDITIONS

SOLV. VISC 2.10(CP)  
SOLV. DENS 0.79(G/CC)  
SAMP. DENS 3.97(G/CC)  
D(CAN) 10.0 (PH)  
D(CIN) 6.10(PH)  
D(CIV) 1.00(PH)  
SPEED 500. (RPM)

• TIME 8 H 7 MIN 36 SEC

• DATA 0.9

TIME ABSORBANCE



• DISTRIBUTION TABLE (BY VOL.)

| D(PH)       | F(%) | P(%)  |
|-------------|------|-------|
| 10.0 -      | 0.0  | 0.0   |
| 10.0 - 9.0  | 4.5  | 4.5   |
| 9.00 - 8.00 | 0.0  | 4.5   |
| 8.00 - 7.00 | 0.0  | 4.5   |
| 7.00 - 6.00 | 0.0  | 4.5   |
| 6.00 - 5.00 | 0.0  | 4.5   |
| 5.00 - 4.00 | 0.0  | 4.5   |
| 4.00 - 3.00 | 5.5  | 10.0  |
| 3.00 - 2.00 | 10.5 | 20.6  |
| 2.00 - 1.00 | 21.0 | 41.5  |
| 1.00 - 0.00 | 51.5 | 100.0 |

D(AVE) 0.57 (PH)

• DISTRIBUTION GRAPH (BY VOL.)

D(PH) F(%)



5/1/89

Administrative Notes

# Analytical Results for C3 HD/LD STUDY - Holes

IBM  
RESEARCH CENTER

ANALYTICAL  
LABORATORY

IBM

Request for Analysis

Use Ball Point Pen

| REQUESTOR <u>T. S. Kiser</u>                                      | PROJECT NO.                  | REQUEST NO.                                |
|---|------------------------------|--|
| DEPARTMENT  | LOCATION                     | ROOM <u>25-225</u> PHONE                   |
| REQUESTOR'S SAMPLE IDENTIFICATION <u>HD ex, LD ex</u>             |                              |  |
| APPROXIMATE COMPOSITION AND HISTORY OF SAMPLE <u>YtBaCu Oxide</u> |                              |  |
| ANALYSES REQUESTED  |                              |  |
| ANALYSIS METHOD   |                              |  |
| <u>low</u>  |                              |  |
| ANALYTICAL RESULTS  |                              |  |
|   | HD                           | LD   |
| wt% "Holes"   | 33.5                         | 34.2                                       |
| wt% Cu  | 22.5                         | 22.0                                       |
|   | 2.21                         | 2.26                                       |
|   | 6.81                         | 4.689                                      |
| $\frac{\text{tot H} - \%}{\% \text{ Cu}}$                         |                              |  |
| Aster Reox: 11Dox   | 28.7                         | wt% Cu ← 25.6                              |
| pure @ 500C   | 36                           | holes                                      |
| DATE SUBMITTED <u>3/22/89</u>                                     | DATE REPORTED <u>3/24/89</u> | NOTES/BOOK REFERENCE <u>7/11/84 p. 121</u> |
| ANALYST <u>T. S. Kiser</u>  | APPROVAL                     |  |

No

5/2/89

Administrative Notes

Recalculation Pre HD, LD values w/ 28.7% C

$$\text{HD holes } 33.5 \therefore \frac{33.5 - 28.7}{28.7} = 0.167$$

$$2 + 0.167 = 2.167 (3) = +6.50$$

$$\frac{+7}{13.50} / 2 = 6.75 \Rightarrow \text{y Ba}_2\text{Cu}_3 \text{ } ^{2.167} 0.675$$

$$\text{LD } \frac{34.2 - 28.7}{28.7} = 0.192 \quad 2.192 (3) = 6.58$$

$$\frac{+7}{13.58} / 2 = 6.79$$

$$\therefore \text{y Ba}_2\text{Cu}_3 \text{ } ^{2.192} 0.679$$

with original anal. C values

$$\text{HD } \frac{33.5 - 27.5}{27.5} = 0.22 \quad 2.22 (3) = 6.66 + 7 = 13.66 / 2 = 6.83$$

$$\text{LD } \frac{34.2 - 27.0}{27} = 0.27 \quad 2.27 (3) = 6.81 + 7 = 13.81 / 2 = 6.90(5)$$

$$\text{w/ ave } 27.5 + 27 = 27.25$$

$$\text{LD } \frac{34.2 - 27.25}{27.25} = 0.25(5) \quad 2.255 (3) = 6.765 = 13.765 / 2 = 6.88$$

$$\text{HD } \frac{33.5 - 27.25}{27.25} = 0.23 \quad 2.23 (3) = 6.69 \text{ } \left( \begin{array}{l} 6.845 \\ 6. \end{array} \right)$$

| Composition<br># | Rel Pellet<br>density (%) | Actual<br>density | Green<br>Rel<br>δ | Green<br>act<br>δ |
|------------------|---------------------------|-------------------|-------------------|-------------------|
| 1                | 84 (90.8)                 | 5.34              | 62.9              | 4.0               |
| 2                | 98.9                      | 5.95              | 61.5              | 3.90              |
| 3                | 71                        | 4.52              | 60-               | 3.82              |
| 4                | 77.8                      | 4.95              | 62                | 3.93              |
| 5                | 87 (91)                   | 5.54              | 63.9              | 4.03              |

\* after 1h sinter @ 950C



00-IBM YORKTOWN

|    | DATE  | TIME  | TO/FROM      | MODE  | MIN/SEC | PGS | CMD# | STATUS |
|----|-------|-------|--------------|-------|---------|-----|------|--------|
| 32 | 12/16 | 16:06 | 917033053599 | EC--S | 06'40"  | 025 | 124  | OK     |

**IBM Corporation**

Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, NY 10598  
FAX: T/L 862-3281  
or (914) 945-3291

## FACSIMILE

DATE: 12/16/98 NO. OF PAGES TO FOLLOW: 24

TO: Examiner M. Kopeck  
NAME: Examiner M. Kopeck

ADDRESS: USPTO- Group 1105

PHONE NO. 703-308-1088

FAX NO. 703-305-3599

FROM: Daniel Morris  
NAME: Daniel Morris

PHONE NO. 703-945-3217

LOCATION: IBM Yorktown

CONTACT #: 914-945-3243

CLASSIFICATION:

☐ IBM CONFIDENTIAL  
☐ PERSONAL

☐ IBM INTERNAL USE ONLY  
☐ UNCLASSIFIED

MESSAGE: Also sent Affidavits of Nityi,  
Tsuei and Ling for B2 case  
dated 12/15/98

THIS MESSAGE IS INTENDED ONLY FOR THE USE OF THE INDIVIDUAL OR ENTITY TO WHICH IT IS ADDRESSED. AND MAY CONTAIN INFORMATION THAT IS PRIVILEGED, CONFIDENTIAL AND EXEMPT FROM DISCLOSURE UNDER APPLICABLE LAW. IF THE READER OF THIS MESSAGE IS NOT THE INTENDED RECIPIENT, OR THE EMPLOYEE OR AGENT RESPONSIBLE FOR DELIVERING THE MESSAGE TO THE INTENDED RECIPIENT, YOU ARE HEREBY NOTIFIED THAT ANY DISSEMINATION, DISTRIBUTION OR COPYING OF THIS COMMUNICATION IS STRICTLY PROHIBITED. IF YOU HAVE RECEIVED THIS COMMUNICATION IN ERROR, PLEASE NOTIFY US IMMEDIATELY BY TELEPHONE AND RETURN THE

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 16, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

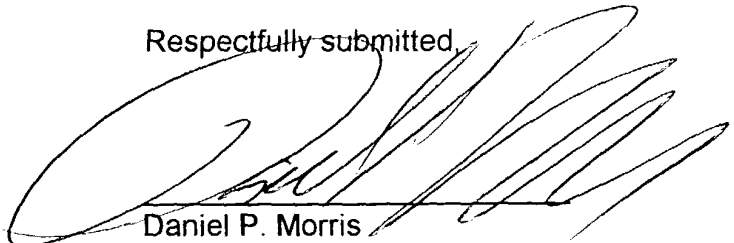
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATION OF TRANSMISSION PURSUANT TO 37 CFR 1.8**

I hereby certify that this paper is being facsimile transmitted under Rule CFR  
1.6(d) to the U.S. Patent and Trademark Office on the date shown above.

Respectfully submitted,

A large, stylized handwritten signature in black ink, appearing to read 'Daniel P. Morris', is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

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Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AMENDMENT AFTER FINAL REJECTION**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

In the referenced final Office Action, the Examiner refers to three affidavits (of Mitzi, Tsuei and Dinger) submitted by applicants to overcome the rejection under 35-USC 112 for a lack of enablement. The Examiner's comments are at (paragraph (d)(iv) page 7, 5 lines from the bottom to page 8, 4 lines from the bottom. The Examiner states:

(d)(iv)(1) "Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make these superconductors without undue experimentation."

(d)(iv)(2) "Those affidavits do not overcome the non-enablement rejection."

(d)(iv)(3) "Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made."

Moreover, in applicant's response dated May 14, 1998, applicants refer to Poole et al. which states at page 59 thereof "[c]opper oxide superconductors with a parity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials" (see applicant's response for the entire text that is quoted and Attachment A thereof for copies of relevant pages from Pool et al.)

In response the Examiner states:

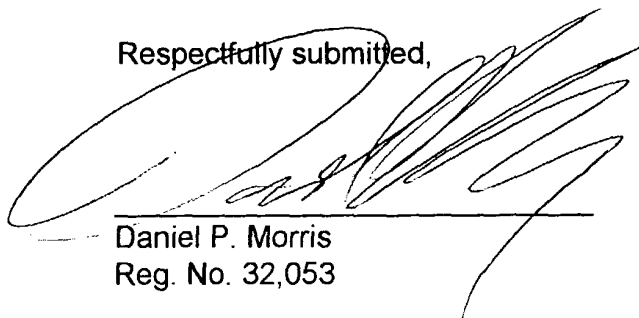
(1) Initially, however, it should be noted that the Poole article was published *after* the priority date presently claimed. As such, it does not provide evidence of the state of the art *at the time* the presently claimed invention was made.

(2) Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting condition.

Applicants respectfully disagree with the Examiner. In further support of applicants position that all their claims are fully enabled, applicant's submit the amended affidavit of Mitzi, Tsuei and Dinger which provides a list of books and articles published prior to applicants filing date showing the general principles of ceramic science used by applicants and which are used as stated by Poole et al. to make the high Tc

superconductors taught and claimed by applicants which "are not difficult to synthesize."

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Daniel P. Morris", is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Chang C. Tsuei, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Mechanical Engineering from National Taiwan University (1960) and M. S. and PhD. degrees, in Material Science (1963, 1966) respectively from California Institute of Technology.

That I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1973 to the present. (See attached Exhibit A for other professional employment history.)

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1973 to the present.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of  
YO987-074BY

✓

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasso, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+*}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_{5-0.13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Chang C. Tsuei  
Chang C. Tsuei

Sworn to before me this 16<sup>th</sup> day of December, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

YO987-074BY



CHANG C. TSUEI

Education

California Institute of Technology, M.S. (1963), Ph.D. (1966)

National Taiwan University, B.S. (1960)

Professional Employment

1993 - present - Research Staff Member

1983 - 1993 - Manager, Physics of Structured Materials

1979 - 1983 - Manager, Physics of Amorphous Materials

1974 - 1975 - Acting Manager, Superconductivity

1973 - 1979 - Research Staff Member

Harvard University: 1980 (Summer)

Visiting Scholar in Applied Physics

Stanford University: 1982 (Sept.) - 1983 (April)

Visiting Scholar in Applied Physics

California Institute of Technology

1972 - 1973 - Senior Research Associate in Applied Physics

1969 - 1972 - Senior Research Fellow in Materials Science

1966 - 1969 - Research Fellow in Materials Science

Exhibit A

YO987-074BY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, David B. Mitzi, being duly sworn, do hereby depose and state:

That I received a B. S. E. degree in Electrical Engineering/Engineering Physics (1985) from Princeton University and a PhD. degree, in Applied Physics (1990) from Stanford University, California.

That I have worked as a research staff member in Solid State Chemistry at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1990 to the present.

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1990 to the present.

That I have reviewed the above-identified patent application and that I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and

YO987-074BY

✓

Muller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.


The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By:   
David B. Mitzi

Sworn to before me this 15<sup>th</sup> day of December, 1998

  
Notary Public

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4886676  
Qualified in Westchester County  
Commission Expires March 16, 1999

YO987-074BY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

: Date: December 15, 1998

Serial No. 08/303,561

: Group Art Unit: 1105

Filed: September 9, 1994

: Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Timothy Dinger, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M. S. degree (1983) and a PhD. degree (1986), both in Material Science from the University of California at Berkley.

That I have worked as a research staff member in Material Science at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1986 to the present.

That I have worked in the fabrication of and characterization of high temperature superconductor materials from 1987 to 1991.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of

YO987-074BY

✓

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar way, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasso, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

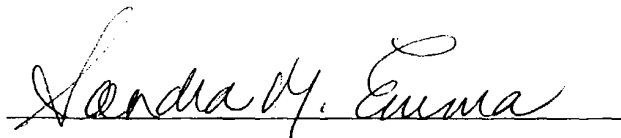
- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_{5-0.134}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By:



Timothy Dinger

Sworn to before me this 16<sup>th</sup> day of December, 1998



Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

YO987-074BY

\*\* TX STATUS REPORT \*\*

AS OF DEC 15 '98 15:43 PAGE.01

|    | DATE  | TIME  | TO/FROM      | MODE  | MIN/SEC | PGS | CMD# | STATUS |
|----|-------|-------|--------------|-------|---------|-----|------|--------|
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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

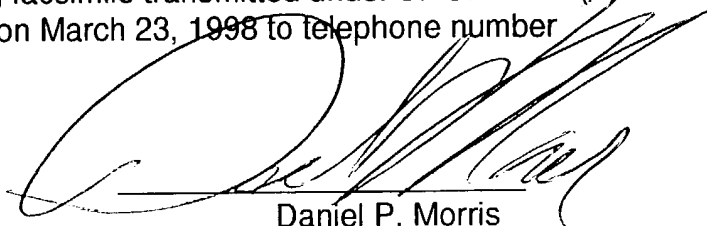
Examiner: M. Kopeck

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under 37 CFR 1.61(d) to the U.S. Patent and Trademark Office on March 23, 1998 to telephone number 703-305-3599.



Daniel P. Morris  
Reg. No. 32,053

**AMENDMENT AFTER FINAL REJECTION UNDER 37 CFR 1.116**

Attached is an affidavit under 37 CFR 1.132 of Dr. James W. Leonard, IBM research librarian. Dr. Leonard did a search of articles referencing applicants article J. G. Bednorz and K. A. Muller, Zeitschrift fur Physik B- Condensed Matter, **64**, pp. 189-193 (Sept. 1986) which is incorporated by reference in the specification at page 6, lines 8-10. As stated at page 6 this article is the basis for applicants invention. More than 5800 articles have referenced applicants' article. This is evidence that applicants' teaching in the present application has motivated persons of skill in the art to work in

YO987-074BY

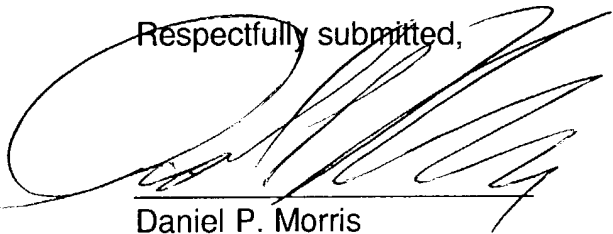
the field of high  $T_c$  superconductivity and that applicants teaching has fully enabled the invention of their claims. All these articles citing applicants' article acknowledge that their work is based on applicants' teaching. Thus applicants respectfully request the withdrawal of the rejection of applicants' claims under 35 USC 112 as lacking enablement.

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598  
(914) 945-3217

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AFFIDAVIT UNDER 37 CFR 1.132**

Sir:

I, James W. Leonard, being duly sworn, do hereby depose and state:

I received a A.B. degree in Physics from the University of California at Santa Barbara (1962), and a M.S. and PhD. degree in Physics (1968) from the University of Oregon, Eugene, and an M.L.S. in Library Science from the University of Western Ontario (1972), London.

I have worked as a science librarian in the Thomas J. Watson Research Center from 1978 to the present. On December 2, 1998, I did a citation search in the SciSearch database on the Dialog on line system of the article J. G. Bednorz and K. A. Muller, Zeitschrift fur Physik B- Condensed Matter, **64** , pp. 189-193 (Sept. 1986). The result

of that search is below. There are a total of 5689 articles which refer to 1986 article of Bednorz and Muller: 1 in 1986, 839 in 1987, 1163 in 1988, 793 in 1989, 594 in 1989 and the remainder in the years from 1990 to the present.

### SEARCH RESULTS

SYSTEM:OS - DIALOG OneSearch  
File 434:SciSearch(R) Cited Ref Sci 1974-1989/Dec  
(c) 1998 Inst for Sci Info  
File 34:SciSearch(R) Cited Ref Sci 1990-1998/Nov W4  
(c) 1998 Inst for Sci Info

| Set | Items | Description                       |
|-----|-------|-----------------------------------|
| S1  | 5689  | CR=BEDNORZ JG, 1986, V64, P189, ? |
| S2  | 1     | S1 AND PY=1986                    |
| S3  | 839   | S1 AND PY=1987                    |
| S4  | 1163  | S1 AND PY=1988                    |
| S5  | 793   | S1 AND PY=1989                    |
| S6  | 594   | S1 AND PY=1990                    |

By: James W. Leonard  
James W. Leonard

Sworn to before me this 15 day of December, 19 98.

[Signature]  
Notary Public

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 408676  
Qualified in Westchester County  
Commission Expires March 16, 19 99

Filing: Affidavit Under 37 CFR 1.132 of Thomas M. Shaw, Publication list of T.M. Shaw, Copies of books (chapters) referenced on page 3 of Affidavit (to be hand-carried by WAIRPL) to PTO

PLEASE STAMP & RETURN TO US

In re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No08/303,561 : Filed: 09. X0987-074BY 2. 1. 1. DPM

Received in the U.S. Patent & Trademark Office:

No. of pages of specification: No. of pages of claims

No. of claims of independent

Declaration is attached to specification.

All fees are charged to our Account No. 00-0469

12/15/98

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AFFIDAVIT UNDER 37 CFR 1.132**

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y.  
from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications. I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.



3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.

4) Thermal Behaviour of Compositions in the Systems  $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Thomas M. Shaw  
Thomas M. Shaw

Sworn to before me this 14th day of December, 1998.

Sandra M. Emma  
Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

Filing: Amendment After Fin Filing: Amendment After Final (to be hand-carried by WAIPL to the PTO) the PTO)

PLEASE STAMP

PLEASE STAMP & RETURN TO US

in re application of: J. Be in re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE CO For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION ...

Serial No. 08/303,561; Docket Serial No. 08/303,561; Docket No. X0987-074BY Atty.: DPM

Received in the U.S. Patent, Received in the U.S. Patent & Trademark Office:

No. of pages of specification No. of pages of specification No. of pages of claims

No. of sheets of drawings: No. of sheets of drawings: No.

Declaration is attached to an Declaration is attached to specification.

**ATTI fees** are charged to our / **ATTI fees** are charged to our Account No. 09-0468

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AMENDMENT AFTER FINAL REJECTION**

Sir:

In response to the Office Action dated June 25, 1998, please consider the following:

**REMARKS**

In the referenced final Office Action, the Examiner refers to three affidavits (of Mitzi, Tsuei and Dinger) submitted by applicants to overcome the rejection under 35 USC 112 for a lack of enablement. The Examiner's comments are at (paragraph (d)(iv) page 7, 5 lines from the bottom to page 8, 4 lines from the bottom. The Examiner states:

(d)(iv)(1) "Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make these superconductors without undue experimentation."

(d)(iv)(2) "Those affidavits do not overcome the non-enablement rejection."

(d)(iv)(3) "Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made."

Moreover, in applicant's response dated May 14, 1998, applicants refer to Poole et al. which states at page 59 thereof "[c]opper oxide superconductors with a parity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials" (see applicant's response for the entire text that is quoted and Attachment A thereof for copies of relevant pages from Pool et al.)

In response the Examiner states:

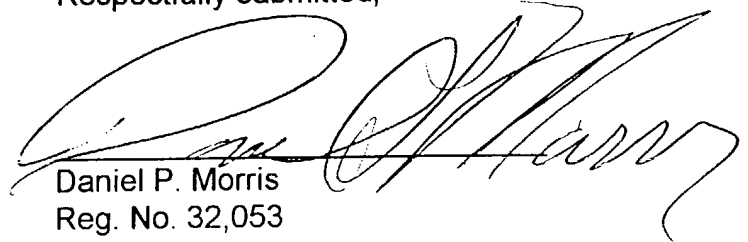
(1) Initially, however, it should be noted that the Poole article was published *after* the priority date presently claimed. As such, it does not provide evidence of the state of the art *at the time* the presently claimed invention was made.

(2) Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting condition.

Applicants respectfully disagree with the Examiner. In further support of applicants position that all their claims are fully enabled, applicant's submit the attached affidavit of Thomas M. Shaw, an expert in ceramic science who agrees with the affidavit of Mitzi, Tsuei and Dinger and provides a list of books and articles published prior to applicants filing date showing the general principles of ceramic science used by applicants and

which are used as stated by Poole et al. to make the high Tc superconductors taught and claimed by applicants which "are not difficult to synthesize."

Respectfully submitted,



Daniel P. Morris  
Reg. No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598  
(914) 945-3217

# PUBLICATIONS T.M.SHAW

1. D.R.Clarke and T.M.Shaw, D.P.Thompson, "Direct Observation of the Polytype Periodicities in the Be-Si-O-N System.", J. Mat. Sci. 13 pages 217-219 (1978)
2. T.M. Shaw, "Transmission Electron Microscopy Analysis of Complex Nitrogen Ceramics", Proceedings of the 9th International Congress on Electron Microscopy, Toronto. Ed J.M. Sturgess (Microscopical Society of Canada, 1978). Vol. 1 Page 258.
3. D.R. Clarke and T.M. Shaw, "polytypism in Magnesium Sialon", in Processing of Crystalline Ceramics (Materials Science Research Vol. 11), Edited by H. Palmour III, R.F. Davis and T.M. Hare., Plenum press 1978.
4. T.M. Shaw and G. Thomas, "Transmission Electron Microscopy: Direct Observation of Crystal structure in Refractory ceramics", Science 202, pages 625-626 (1978)
5. O.L. Krivanek, T.M. Shaw and G. Thomas, "Imaging of Thin Intergranular Phases by High resolution Electron Microscopy", J. Appl. Phys. 50, pages 4223-4227 (1979).
6. O.L. Krivanek T.M. Shaw and G. Thomas, "The Microstructure and Distribution of Impurities in Hot-Pressed and Sintered Silicon Nitrides" J. Amer. Ceram. Soc. 62, pages 585-590 (1979)
7. T.M. Shaw O.L. Krivanek and G. Thomas, "Glass Free Grain Boundaries in Be-Si-N Ceramics", J. Amer. Ceram. Soc. 62, pages 305-306 (1979).
8. T.M. Shaw and G. Thomas, "An Electron Microscopy Study of Crystallography and Phase relationships in the Be-Si-N system", J. Solid State Chem. 33, pages 63-82 (1980).
9. T.M. Shaw and G. Thomas "The crystallization Behavior of a Mg- Si-O-N Glass " in Progress in Nitrogen ceramics, Proceedings of the NATO Advanced Study Institute, Ed F.L.Riley, Martinus Nijhoff (1983).
10. T.M. Shaw and C.B. Carter, "Faceting in Twin Boundaries in Spinel", Scripta Met. 16, pages 1431-1435 (1983).
11. P.E.D. Morgan and T.M. Shaw, "Magnetoplumbite Related Barium Aluminates", Mat. Res Bull. 18, pages 539-542 (1983).
12. P.E.D.Morgan, T.M.Shaw and E.A.Pugar "Ceramics For High Waste Loaded Commercial Radwaste disposal" In Advances in Ceramics, Vol 8, Nuclear Waste Management. Ed G.G.Wicks and W.A.Ross. Published Amer. Ceram. Soc. 1984.
13. P.E.D.Morgan, A.B.Harker, J.F.Flintoff, T.M.Shaw, and D.R.Clarke "Developments in SRP "composite" Defense Ceramic Radwaste Forms" In Advances in Ceramics, Vol 8, Nuclear Waste Management. Ed G.G.Wicks and W.A.Ross. Published Amer. Ceram. Soc. 1984.
14. T.M.Shaw, G.Thomas and R.E.Loehman "The formation and microstructure of Mg-Si-O-N Glasses" J. Amer. Ceram. Soc. Nov 1984.
15. T.M.Shaw, J.W.Steeds and D.R.Clarke "Fault Structures in CVD silicon nitride" Proceedings of M.R.S. Symposia on the Electron Microscopy of Materials. North Holland 1984.



UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

| SERIAL NUMBER | FILING DATE | FIRST NAMED APPLICANT | ATTORNEY DOCKET NO. |
|---------------|-------------|-----------------------|---------------------|
| 08/303,561    | 09/09/94    | BEDNORZ               | J Y0987074BY        |

DANIEL P MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

IM51/1214

| EXAMINER |              |
|----------|--------------|
| KOPEC, M |              |
| ART UNIT | PAPER NUMBER |
| 1751     | 68           |

DATE MAILED: 12/14/98

Below is a communication from the EXAMINER in charge of this application  
COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

DCE 11/25/98

☒ THE PERIOD FOR RESPONSE:

- ☒ is extended to run 5 mos. from the date of the Final Rejection
- ☐ continues to run \_\_\_\_\_ from the date of the Final Rejection
- ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition, and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date that the shortened statutory period for response expires as set forth above.

☐ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 11/25/98, has been considered with the following affect, but it is not deemed to place the application in condition for allowance:

1. ☒ The proposed amendments to the claim and/or specification will not be entered and the final rejection stands because:

- a. ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.
- b. ☐ They raise new issues that would require further consideration and/or search. (See Note).
- c. ☐ They raise the issue of new matter. (See Note).
- d. ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.
- e. ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

NOTE: Added & Amended claims are of improper form (e.g. claims 126, 142, 145)  
SEE 37 CFR 1.121 and MPEP 714.22  
Claims meeting the requirements of 37 CFR 1.121 will be entered & considered.

2. ☐ Newly proposed or amended claims \_\_\_\_\_ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☐ Upon the filing of an appeal, the proposed amendment ☐ will be ☐ will not be, entered and the status of the claims in this application would be as follows:

Allowed claims: \_\_\_\_\_

Claims objected to: \_\_\_\_\_

Claims rejected: \_\_\_\_\_

However;

- a. ☐ The rejection of claims \_\_\_\_\_ on references is deemed to be overcome by applicant's response.
- b. ☐ The rejection of claims \_\_\_\_\_ on non-reference grounds only is deemed to be overcome by applicant's response.

4. ☐ The affidavit, exhibit or request for reconsideration has been considered but does not overcome the rejection.

5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficient reasons why it was not earlier presented.

☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

☐ Other

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## ***FACSIMILE***

DATE: Dec. 14, 1998 NO. OF PAGES TO FOLLOW: 4

TO:  
NAME: Examiner M. Kopeck

ADDRESS: USPTO - Group 1105

PHONE NO. 703-308-1088

FAX NO. 703-305-3599

FROM:  
NAME: Daniel Morris

PHONE NO. 914-945-3217

LOCATION: IBM - Yorktown

CONTACT #: 914-945-3243

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Amendment dated Dec. 10, 1998, Serial # 08/303,561  
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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 10, 1998

Serial No. 08/303,561

Group Art Unit: 1105

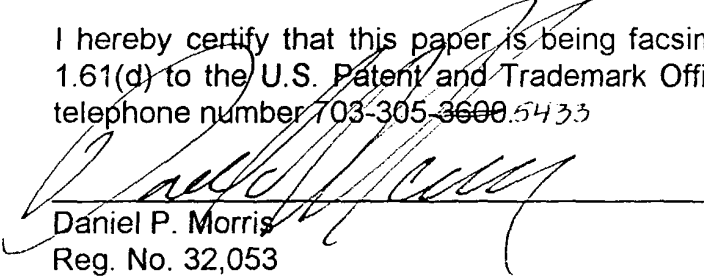
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under Rule CFR  
1.61(d) to the U.S. Patent and Trademark Office on the date shown above To  
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Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

120. (Amended) A method comprising the steps of:

forming a composition including a transition metal, oxygen and [any] an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

123. (Amended) A superconductive method for conducting an electric current

essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $[T] T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and



(c) causing an electric current to flow in the superconductor element.

129. (Amended) A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition [~~while~~] with said phase exhibiting said superconductivity.

130. (Amended). A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide [~~being~~] at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

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CP 3

in re application of **GROUP 1700** Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No. 08/303,561; Docket No. YO987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification \_\_\_\_\_: No. of pages of claims \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

**NY** fees are charged to our Account No. 09-0468

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WAIPL)

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in re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No. 08/303,561; Doctee No. Y0987-074BY A107; DPM

Received in the U.S. Patent & Trademark Office:

No. of pages of specification:           ; No. of pages of claims           

No. of sheets of drawings:           

Declaration is attached to specification.

**All fees are charged to our Account No. 09-0462**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 11, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

**REMARKS**

Reconsideration is respectfully requested in view of any changes to the claims  
and the remarks herein. Please contact the undersigned to conduct a telephone  
interview in accordance with MPEP 713.01 to resolve any remaining  
requirements and/or issues prior to sending another Office Action. Relevant  
portions of MPEP 713.01 are included on the signature page of this amendment.

In view of the changes to the claims and the remarks herein, the Examiner is  
respectfully requested to reconsider the above-identified application. If the  
Examiner wishes to discuss the application further, or if additional information

would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Claims 86-87, 96-108, 112, 113, 115, 117, 118, 122 and 123 rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

The Examiner states that "with respect to claims 86-87 and 96-108, the terms 'layer-type', 'perovskite-like' are unclear because the 'type' or 'like' terms are deemed to be indefinite. Terms such as 'like', 'similar' and 'type' are indefinite." Applicants respectfully disagree.

Attachment A is the result of a Lexis search done by the undersigned attorney. This search shows the term "rare earth like" or "rare earth and the like" used in 68 US patents. The section of the 68 patents where these terms appear are printed using the "KWICK" function of Lexis. Attachment B is the result of a Lexis search done by the undersigned attorney. This search shows the term "rare earth like" used in the claims of 4 issued US patents. The sections of the claims of the 4 patents where this term appears in the claims are printed using the "KWICK" function of Lexis. Consequently, the term "rare earth like" is a term used in the art, understood by a person of skill in the art and recognized as a definite term by the USPTO for use in US patent claims.

The term "perovskite-like" or "perovskite-type" is commonly used in the art. Attachment C is the result of a Lexis search done by the undersigned attorney. This search shows that the terms "perovskite like" and "supercond!" (the "!" represents any combination of letters) are used in 107 US patents. The sections of the 107 patents where these terms appear are printed using the "KWICK" function of Lexis. Attachment D is the result of a Lexis search done by the

undersigned attorney. This search shows the terms "perovskite like" or "perovskite type" used in the claims of two issued US patents. The sections of the claims of the 2 patents where this term appears in the claims are printed using the "KWICK" function of Lexis. Attachment E is a copy of the first page of Chapter 2 of the book "Perovskites and High T<sub>c</sub> Superconductors" by F. S. Galasso, Gordon and Breach Scientific Publishers, 1990. Chapter 2 is entitled "Structure of Perovskite-type Compounds". Attachment F is a copy of page 78 of the book by C. Poole, Jr. et al.. Page 78 is the beginning of the section entitled "D. Perovskite-type Superconducting Structures". The first paragraph of the section states "[i]n their first report on high-temperature superconductors Bednorz and Muller [(the applicants)] referred to their samples as 'metallic, oxygen deficient...perovskite like mixed valent copper compounds.' Subsequent work has confirmed that the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects" (added). Attachment G is a copy of pages 72 to 86 from Poole et al. In Chapter VI on "Crystallographic Structures" Poole et al. states at page 73 "[m]uch has been said about the oxide superconductor compounds being **perovskite types**, so we will begin with a description of the perovskite structure." (emphasis added) Poole further states at page 74 in Section 4 entitled "Tetragonal Form" that "[a]t room temperature barium titanate is tetragonal ... which is close to cubic." Poole further states at page 74 in Section 3 entitled "Orthorhombic Form" that "[w]hen barium titanate is cooled below 5° C it undergoes a transition with a further lowering of the symmetry to the orthorhombic space group." Consequently, the terms "perovskite like" or "perovskite type" are terms used in the art and recognized as a definite by the USPTO for use in US patent claims. (It is noted that this passage also shows that the terminology "mixed valent copper compounds" is used and understood in the art.

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

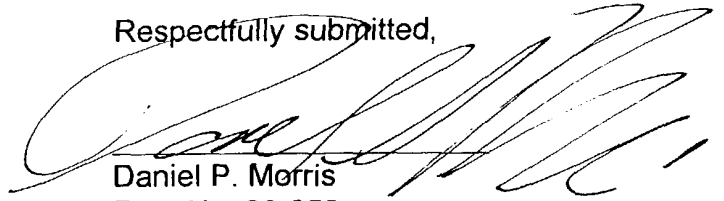
If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,



Daniel P. Morris  
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IBM CORPORATION  
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Yorktown Heights, New York 10598



Attachment A

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LEVEL 1... 68

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\*\*\*\*\*06068\*\*\*\*\*  
LEVEL 1 - 1 OF 68 PATENTS

5,670,078

<=2> GET 1st DRAWING SHEET OF 7

Sep. 23, 1997

Magnetic and nonmagnetic particles and fluid, methods of  
making and methods of using the same

INVENTOR: Ziolo, Ronald F., Webster, New York

DETDSC:

... described in U.S. Pat. No. 4,474,886 to Ziolo. Examples of the precursor  
ions which may be used includes those derivable from transition metal ions, such  
as iron, cobalt, nickel, manganese, vanadium, chromium, rare earths and the  
like. In the case of a non-magnetic colloid, this may include ions of, for  
example, sulfur, selenium, gold, barium, cadmium, copper, silver, manganese,  
molybdenum, zirconium, gallium, arsenic, indium, tin, ...

... ions which can be incorporated into the resin beads to form both

single-domain and multi-domain magnetic particles include. ... use derivable from transition metal ions, such as iron, cobalt, nickel, manganese, vanadium, chromium, rare earths and the like. These ions generally exist in the form of chlorides of the metal involved such as ferrous chloride, ferric chloride, copper chloride, nickel chloride, and the like. The corresponding iodides, bromides and fluorides may also be suitable. ...

LEVEL 1 - 2 OF 68 PATENTS

5,663,319

Sep. 2, 1997

Probe compositions for chromosome identification and methods

INVENTOR: Bittner, Michael L., Naperville, Illinois  
Morrison, Larry E., DuPage County, Illinois  
Legator, Mona S., Chicago, Illinois

SUM:

... capable of reacting, and a fluorophore group may have already reacted, with a linking group. A fluorescent compound may include an organic chelator which binds a luminescent inorganic ion such as a rare earth like terbium, europium, ruthenium, or the like.

The term "linking compound" or "linking group" as used herein generally refers to a hydrocarbonaceous moiety. A linking compound is capable of reacting, and a linking group may have ...

LEVEL 1 - 3 OF 68 PATENTS

5,601,934

<=2> GET 1st DRAWING SHEET OF 1

Feb. 11, 1997

Memory disk sheet stock and method

INVENTOR: Bartges, Charles W., Delmont, Pennsylvania  
Baumann, Stephen E., Penn Hills, Pennsylvania  
Hyland, Jr., Robert W., Oakmont, Pennsylvania  
Jensen, Craig L., Pittsburgh, Pennsylvania  
Tarcy, Gary P., Plum, Pennsylvania  
Vinnedge, K. Dean, Bettendorf, Iowa  
Skeen, Troy C., Bettendorf, Iowa

DETDISC:

... automatically grouped with this same series of elements even though it often performs the same function as scandium, or other "true" rare earths in an alloy composition. It is believed that minor amounts of still other rare earths, like erbium, thulium, lutetium, ytterbium, or another rare earth "act-alike", like hafnium, may be substituted for, or possibly even combined with scandium (or with each other) in varying quantities to achieve the ...

LEVEL 1 - 4 OF 68 PATENTS

5,593,951

<=2> GET 1st DRAWING SHEET OF 4

Jan. 14, 1997

Epitaxy of high T[C ]superconductors on silicon

INVENTOR: Himpel, Franz J., Mt. Kisco, New York

SUM:

... as well as to understand the basic mechanisms for superconductivity in this class of materials.

A2

Bednorz and Mueller first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure.

Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O ...

DETDISC:

... EMBODIMENTS

A technique is provided for depositing high  $T_c$  superconducting copper-oxide based materials epitaxially on Si (001). Typically, these classes of superconducting materials include a rare earth or rare earth-like element and/or an alkaline earth element. Representative formulas for such materials are the following:

$(A_{1-\chi} B_{\chi})_2 Cu_{\epsilon}$

and

$A_1 B_2 Cu_{30\epsilon}$

where A is a trivalent element ( e.g., ...

... in the art that the present invention applies to epitaxial structures including silicon (001) surfaces and any copper oxide superconductor thereon. Thus, the teaching of this invention can include copper-oxide based compositions having any combinations of rare earth or rare earth-like elements and/or alkaline earth elements as well as copper oxide superconductors which do not contain rare earth elements. Further, it will be apparent to those of skill in the art that the Si (001) surface is ...

LEVEL 1 - 5 OF 68 PATENTS

5,573,574

Nov. 12, 1996

Electrorefined aluminium with a low content of uranium,  
thorium and rare earths

INVENTOR: Leroy, Michel, St. Egreve, France

SUM:

... applications specifies a minimum Al content of above 99.9995%, (and even sometimes above 99.9997%) and a U + Th content of less than 1 ppb, and even sometimes less than 0.3 or 0.1 ppb.

Rare earths, some of which, like samarium, have a significant alpha radioactivity, are also undesirable. By way of example, 10 ppb of natural samarium emits as many alpha particles as 0.1 ppb of uranium 238. The high purity ...

LEVEL 1 - 6 OF 68 PATENTS

5,569,759

<=2> GET 1st DRAWING SHEET OF 25

Oct. 29, 1996

Water soluble texaphyrin metal complex preparation

INVENTOR: Sessler, Jonathan L., Austin, Texas  
Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDISC:

A3

... C), 10.24 (s, 2 H, ArH), 12.23 (s, 2 H, CH=N); UV/VIS: lambda [max]  
]420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> , and Dy< + 3> complexes.

#### EXAMPLE 4

Synthesis of B2T2 TXP, see FIGS. 7A and ...  
LEVEL 1 - 7 OF 68 PATENTS

5,567,564

<=2> GET 1st DRAWING SHEET OF 7

Oct. 22, 1996

Liquid development composition having a colorant comprising  
a stable dispersion of magnetic particles in an aqueous  
medium

INVENTOR: Ziolo, Ronald F., Webster, New York

#### DETDISC:

... described in U.S. Pat. No. 4,474,886 to Ziolo. Examples of the precursor ions which may be used includes those derivable from transition metal ions, such as iron, cobalt, nickel, manganese, vanadium, chromium, rare earths and the like. In the case of a non-magnetic colloid, this may include ions of, for example, sulfur, selenium, gold, barium, cadmium, copper, silver, manganese, molybdenum, zirconium, gallium, arsenic, indium, tin, ...

... ions which can be incorporated into the resin beads to form both single-domain and multidomain magnetic particles include: those derivable from transition metal ions, such as iron, cobalt, nickel, manganese, vanadium, chromium, rare earths and the like. These ions generally exist in the form of chlorides of the metal involved such as ferrous chloride, ferric chloride, copper chloride, nickel chloride, and the like. The corresponding iodides, bromides and fluorides may also be suitable. ...

LEVEL 1 - 8 OF 68 PATENTS

5,554,428

Sep. 10, 1996

Memory disk sheet stock and method

INVENTOR: Bartges, Charles W., Delmont, Pennsylvania  
Hayland, Jr., Robert W., Oakmont, Pennsylvania  
Jensen, Craig J., Pittsburgh, Pennsylvania  
Baumann, Steven F., Penn Hills, Pennsylvania (Rule 47 Application)

#### SUM:

... automatically grouped with this same series of elements even though it often performs the same function as scandium, or other "true" rare earths in an alloy composition. It is believed that minor amounts of still other rare earths, like erbium, thulium, lutetium, ytterbium, or another rare earth "act-alike", like hafnium, may be substituted for, or possibly even combined with scandium (or with each other) in varying quantities to achieve the ...

LEVEL 1 - 9 OF 68 PATENTS

5,504,205

<=2> GET 1st DRAWING SHEET OF 25

Apr. 2, 1996

INVENTOR: Sessler, Jonathan L., Austin, Texas  
Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDISC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N); UV/vis: lambda max 420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> and Dy< + 3> complexes.

EXAMPLE 4

Synthesis of B2T2 TXP, see FIG. 7.

PAGE

LEVEL 1 - 10 OF 68 PATENTS

5,491,224

Feb. 13, 1996

Direct label transaminated DNA probe compositions for chromosome identification and methods for their manufacture

INVENTOR: Bittner, Michael L., 1768 Brookdale Rd., Naperville, Illinois 60563  
Morrison, Larry E., 21 W. 559 Kensington Rd., Glen Ellyn, Illinois 60137  
Legator, Mona S., 6540 N. Francisco, Chicago, Illinois 60645

DETDISC:

... capable of reacting, and a fluorophore group may have already reacted, with a linking group. A fluorescent compound may include an organic chelator which binds a luminescent inorganic ion such as a rare earth like terbium, europium, ruthenium, or the like.

The term "linking compound" or "linking group" as used herein generally refers to a hydrocarbonaceous moiety. A linking compound is capable of reacting, and a linking group may have ...

LEVEL 1 - 11 OF 68 PATENTS

5,475,104

<=2> GET 1st DRAWING SHEET OF 26

Dec. 12, 1995

Water soluble texaphyrin metal complexes for enhancing relaxivity

INVENTOR: Sessler, Jonathan L., Austin, Texas  
Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDISC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N); UV/vis lambda max 420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> and Dy< + 3> complexes.

EXAMPLE 4

Synthesis of B2T2 TXP, see FIGS. 7A and ...

LEVEL 1 - 12 OF 68 PATENTS

5,457,183

A5

<=2> GET 1st DRAWING SHEET OF 51

Oct. 10, 1995

Hydroxylated texaphyrins

INVENTOR: Sessler, Jonathan L., Austin, Texas  
Mody, Tarak D., Sunnyvale, California  
Hemmi, Gregory W., Sunnyvale, California  
Kral, Vladimir, Na Kozaaao, Czechoslovakia

DETDESC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N); UV/vis: lambda max 420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized in a similar manner including the La< + 3> , Nd< + 3> , Sm< + 3> , Eu< + 3> , Gd< + 3> , Dy< + 3> and Tm< + 3> complexes.

PAGE

LEVEL 1 - 13 OF 68 PATENTS

5,451,576

<=2> GET 1st DRAWING SHEET OF 26

Sep. 19, 1995

Tumor imaging and treatment by water soluble texaphyrin  
metal complexes

INVENTOR: Sessler, Jonathan L., Austin, Texas  
Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDESC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N); UV/vis: lambda max 420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> and Dy< + 3> complexes.  
EXAMPLE 4

Synthesis of B2T2 TXP, see FIGS. 7A and ...

LEVEL 1 - 14 OF 68 PATENTS

5,447,906

Sep. 5, 1995

Thin film high TC oxide superconductors and vapor deposition  
methods for making the same

INVENTOR: Chaudhari, Praveen, Briarcliff Manor, New York  
Gambino, Richard J., Yorktown Heights, New York  
Koch, Roger H., Amawalk, New York  
Lacey, James A., Mahopac, New York  
Laibowitz, Robert B., Peekskill, New York  
Viggiano, Joseph M., Wappingers Falls, New York

ABST:

... films are produced by vapor deposition processes using pure metal sources for the metals in the superconducting compositions, where the metals include multi-valent nonmagnetic transition metals, rare earth elements and/or rare earth-like elements and alkaline earth elements. The substrate is exposed to oxygen during vapor deposition, and, after formation of the film, there is at least one annealing step in an oxygen ambient and slow cooling over several

hours to room temperature. The substrates chosen are critical as long as they are not adversely reactive with the superconducting oxide film. Transition metals include Cu, Ni, Ti and V, while the rare earth-like elements include Y, Sc and La. The alkaline earth elements include Ca, Ba and Sr.

SUM:

... material in the last decade, wherein the critical transition temperature  $T_c$  at which the material becomes superconducting was increased substantially.

Bednorz and Mueller described copper oxide material including a rare earth element, or rare earth-like element, where the rare earth element could be substituted for by an alkaline earth element such as Ca, Ba or Sr.

The work of Bednorz and Mueller has led to intensive investigation in many laboratories in ...

... 400 K. and methods for making these films, where the films exhibit perovskite-like structure.

It is another object of this invention to provide transition metal oxide superconductive films including a rare earth element, or rare earth-like element, where the films exhibit superconductivity at temperatures greater than 400 K., and methods for making these films.

It is another object of the present invention to provide films having the nominal composition  $ABO_{3-y}$  or  $ABO_y$  ...

... provide superconductive oxide films having the nominal composition  $AB_2Cu_{3-9-y}$ , and methods for making these films, where the films are superconducting at temperatures in excess of 400 K. and A is a rare earth or rare earth-like element, B is an alkaline earth element, and y is sufficient to satisfy valence demands of the composition.

Pat. No. 5447906, \*

It is another object of the present invention to provide smooth, continuous copper oxide superconducting films having a perovskite-like ...

... films being smooth and continuous and exhibiting substantial compositional uniformity. In particular, the films are comprised of transition metal oxides containing a superconducting phase, and typically include a rare earth element or rare earth-like element. These rare earth-like elements include Y, Sc and La. Additionally, the rare earth or rare earth-like elements can be substituted for by an alkaline earth element selected from the group consisting of Ca, Ba, and Sr. The transition metals are multi-valent, non-magnetic elements selected from the group consisting of ...

DETDISC:

... especially a  $T_c$  in excess of liquid nitrogen temperatures. These films are characterized by the presence of a transition metal oxide and typically by the presence of a rare earth element and/or a rare earth-like element which can be substituted for by an alkaline earth. The transition metal element is a multi-valent nonmagnetic element while the alkaline earth element is selected from the group consisting of Ca, Ba, and Sr. The rare earth-like elements include Y, Sc, and La. The nonmagnetic transition metal is selected from the group consisting of Cu, Ni, Ti, and V. Of these, Cu is the most favorable, yielding film properties which are unique and unexpected.

In the further ...

LEVEL 1 - 15 OF 68 PATENTS

5,439,570

<=2> GET 1st DRAWING SHEET OF 26

Aug. 8, 1995

Water soluble texaphyrin metal complexes for singlet oxygen





INVENTOR: Sessler, Jonathan L., Austin, Texas  
Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDESC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N); UV/vis: lambda max 420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> and Dy< + 3> complexes.

EXAMPLE 4

Synthesis of B2T2 TXP, see FIGS. 7A and ...

LEVEL 1 - 16 OF 68 PATENTS

5,432,171

<=2> GET 1st DRAWING SHEET OF 26

Jul. 11, 1995

Water soluble texaphyrin metal complexes for viral deactivation

INVENTOR: Sessler, Jonathan L., Austin, Texas  
Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDESC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N); UV/vis: lambda max 420.0, 477.5, 730.0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> and Dy< + 3> complexes.

EXAMPLE 4

Synthesis of B2T2 TXP, see FIGS. 7A and ...

LEVEL 1 - 17 OF 68 PATENTS

5,362,582

Nov. 8, 1994

Battery separator

INVENTOR: Chang, Victor S., Ellicott City, Maryland  
Hartwig, Richard C., Laurel, Maryland  
Lundquist, Joseph T., Gilroy, California  
Parham, Marc E., Bedford, Massachusetts  
Kung, James K., Lexington, Massachusetts  
Avtges, James A., Belmont, Massachusetts  
Laccetti, Anthony J., North Andover, Massachusetts

SUM:

... say the particulate filler must be inert with respect to such end use battery environment. Therefore, alkali insoluble particulate such as zirconia and titanium dioxide (preferred), oxides, hydroxides and carbonates of calcium, magnesium, iron, rare earth and the like should be used only in sheet products which ultimately are formed into battery separators for alkaline batteries. Similarly, acid insoluble particulates such as silica (a precipitated silica is preferred), and the like should be ...

LEVEL 1 - 18 OF 68 PATENTS

5,358,659

<=2> GET 1st DRAWING SHEET OF 5

Oct. 25, 1994

Magnetic materials with single-domain and multidomain  
crystallites and a method of preparation

INVENTOR: Ziolo, Ronald F., Webster, New York

DETDESC:

... Ions which can be incorporated into the resin beads to form both single-domain and multidomain magnetic particles include: those derivable from transition metal ions, such as iron, cobalt, nickel, manganese, vanadium, chromium, rare earths and the like. These ions generally exist in the form of chlorides of the metal involved such as ferrous chloride, ferric chloride, copper chloride, nickel chloride, and the like. The corresponding iodides, bromides and fluorides may also be suitable. ...

PAGE 20

LEVEL 1 - 19 OF 68 PATENTS

5,322,756

<=2> GET 1st DRAWING SHEET OF 3

Jun. 21, 1994

Magnetic fluids and method of preparation

INVENTOR: Ziolo, Ronald F., Webster, New York

DETDESC:

... several different ions including ferrous or ferric ions. Examples of the precursor ions which may be used includes those derivable from transition metal ions, such as iron, cobalt, nickel, manganese, vanadium, chromium, rare earths and the like. These ions generally exist in the form of chlorides of the metal involved, such as ferrous chloride, ferric chloride, copper chloride, nickel chloride, and the like. The corresponding iodides, bromides and fluorides may also be suitable. ....

LEVEL 1 - 20 OF 68 PATENTS

5,304,966

<=2> GET 1st DRAWING SHEET OF 4

Apr. 19, 1994

Method of adjusting a frequency response in a  
three-conductor type filter device

INVENTOR: Hino, Seigo, Nagoya, Japan  
Ito, Kenji, Nagoya, Japan

SUM:

... each other. Each of the dielectric substrates 1 and 2 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 1 is provided with an external ground conducting layer 3 on the peripheral portion and bottom surface thereof. Similarly, the upper dielectric substrate 2 is provided with an external ground conducting layer 4 on the ...

DETDESC:

... assembling of the filter. Each of the dielectric substrates 21 and 22 may be of dielectric ceramic material having a high dielectric constant and a lower

dielectric loss such as  $\text{BaO-TiO}_2$ ,  $\text{BaO-TiO}_2$ -rare earth or the like. The lower dielectric substrate 21 is provided with an external ground conductor layer 23 on the peripheral portion and outer surface thereof. Similarly, the upper dielectric substrate 22 is provided with an external ground conductor layer 24 on the ...

LEVEL 1 - 21 OF 68 PATENTS

5,296,458

<=2> GET 1st DRAWING SHEET OF 4

Mar. 22, 1994

Epitaxy of high  $T_c$  superconducting films on (001) silicon surface

INVENTOR: Himpel, Franz J., Mt. Kisco, New York

SUM:

... as well as to understand the basic mechanisms for superconductivity in this class of materials.

Bednorz and Mueller first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure. Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O ...

DETDISC:

... EMBODIMENTS

A technique is provided for depositing high  $T_c$  superconducting copper-oxide based materials epitaxially on Si (001). Typically, these classes of superconducting materials include a rare earth or rare earth-like element and/or an alkaline earth element. Representative formulas for such materials are the following:

$(A_{1-x}B_x)_2CuO_4$  - epsilon and  $AlB_2Cu_3O_{7-\epsilon}$

where A is a trivalent element (e.g., La, Y, and ...

... in the art that the present invention applies to epitaxial structures including silicon (001) surfaces and any copper oxide superconductor thereon. Thus, the teaching of this invention can include copper-oxide based compositions having any combinations of rare earth or rare earth-like elements and/or alkaline earth elements as well as copper oxide superconductors which do not contain rare earth elements. Further, it will be apparent to those of skill in the art that the Si (001) surface is ...

LEVEL 1 - 22 OF 68 PATENTS

5,291,162

<=2> GET 1st DRAWING SHEET OF 7

Mar. 1, 1994

Method of adjusting frequency response in a microwave strip-line filter device

INVENTOR: Ito, Kenji, Nagoya, Japan  
Shimizu, Hiroyuki, Nagoya, Japan  
Oguchi, Hotaka, Nagoya, Japan

SUM:

... type which comprises a pair of dielectric substrates 1a and 1b made of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as  $\text{BaO-TiO}_2$  or  $\text{BaO-TiO}_2$ -rare earth or the like, the

dielectric substrates 1a and 1b being stacked to each other. The dielectric substrates 1a and 1b are provided with external ground conducting layers 2a and 2b on the peripheral portion and bottom surface thereof, respectively. On the upper ...

DETDISC:

... assembling of the filter. Each of the dielectric substrates 11 and 12 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 11 is provided with an external ground conducting layer 13 on the peripheral portion and outer surface thereof. Similarly, the upper dielectric substrate 12 is provided with an external ground conducting layer 14 on the ...

... a pair of piezoelectric substrates 11 and 12 each of which may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The dielectric substrates 11 and 12 are provided with external ground conducting layers 13 and 14 on the peripheral portions and outer surfaces thereof, respectively. These ground conducting layers 13 and 14 may be formed by ...

LEVEL 1 - 23 OF 68 PATENTS

5,278,140

<=2> GET 1st DRAWING SHEET OF 5

Jan. 11, 1994

Method for forming grain boundary junction devices using  
high T<sub>c</sub> superconductors

INVENTOR: Chaudhari, Praveen, Briarcliff Manor, New York  
Chi, Cheng-Chung J., Yorktown Heights, New York  
Dimos, Duane B., Montclair, New Jersey  
Mannhart, Jochen D., Metzingen, New York, Federal Republic of Germany  
Tsuei, Chang C., Chappaqua, New York

SUM:

... as well as to understand the basic mechanisms for superconductivity in this class of materials.

Bednorz and Mueller first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure. Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O ...

... excess of about 300 K are generally known as "high T<sub>c</sub> superconductors", and will be referred to in that manner throughout the specification. This designation is meant to include both the materials having rare earth or rare earth-like elements in their crystalline structure, as well as the more recently reported materials which do not contain rare earth or rare earth-like elements. Generally, all these materials are copper oxide based superconductors having Cu-O planes that appear to be primarily responsible for carrying the supercurrents, where the copper oxide planes are separate or in groups separated by the ...

LEVEL 1 - 24 OF 68 PATENTS

5,252,720

<=2> GET 1st DRAWING SHEET OF 25

Oct. 12, 1993

Metal complexes of water soluble texaphyrins

INVENTOR: Sessler, Jonathan L., Austin, Texas

2 All

Hemmi, Gregory W., Austin, Texas  
Mody, Tarak D., Austin, Texas

DETDESC:

... 2H, CH=C), 10.24 (s, 2H, ArH), 12.23 (s, 2H, CH=N) ; UV/vis: lambda max 420.0, 477.5, 730. 0; FAB MS M< + > 811.

Other lanthanide and rare earth-like metal complexes may be synthesized including the Gd< + 3> , Lu< + 3> , La< + 3> , In< + 3> and Dy< + 3> complexes.

EXAMPLE 4

Synthesis of B2T2 TXP, see FIG. 7

PAGE

...  
LEVEL 1 - 25 OF 68 PATENTS

5,235,298

<=2> GET 1st DRAWING SHEET OF 2

Aug. 10, 1993

Temperature compensated stripline filter for microwaves

INVENTOR: Banno, Hisao, Nagoya, Japan  
Nishiki, Masahiro, Nagoya, Japan

SUM:

... 4,785,271 and Japanese Patent Prepublication No. 62-263702.

With the microwave stripline filter of the abovementioned type, generally, each dielectric ceramic substrate is made of ceramic material such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like.

However, there is disadvantage that the commonly used ceramic material has a resonant frequency which is decreased as the temperature is risen because the temperature coefficient of the resonant frequency is of a negative characteristic.

It is therefore an object of the present invention to provide a stripline ...  
LEVEL 1 - 26 OF 68 PATENTS

5,188,809

<=2> GET 1st DRAWING SHEET OF 4

Feb. 23, 1993

Method for separating coke from a feed mixture containing zirconium and radioactive materials by flotation process

INVENTOR: Crocker, William A., Salem, Oregon  
Haygarth, John C., Corvallis, Oregon  
Riesen, Jon A., Albany, Oregon  
Peterson, John R., Salem, Oregon

DETDESC:

... radium removal.

b) Sodium sulfate or any other source of soluble sulfate is then added in excess of the concentration of the barium plus radium ion equivalents and any other cations which might combine with the sulfate ions, i.e. calcium, rare earths, or the like. If the solution is cold, it should be heated and a digestion allowed to take place which can range from a fairly short time up to hours or days. The preferred digestion period would be a few hours with ...

LEVEL 1 - 27 OF 68 PATENTS

&lt;=2&gt; GET 1st DRAWING SHEET OF 5

Nov. 10, 1992

Grain boundary junction devices using high T c  
superconductors

INVENTOR: Chaudhari, Praveen, Briarcliff Manor, New York  
 Chi, Cheng-Chung J., Yorktown Heights, New York  
 Dimos, Duane B., Upper Montclair, New Jersey  
 Mannhart, Jochen D., Metzingen, New York, Federal Republic of Germany  
 Tsuei, Chang C., Chappaqua, New York

## SUM:

... as well as to understand the basic mechanisms for superconductivity in this class of materials.

Bednorz and Mueller first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure. Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O ...

... excess of about 300 K. are generally known as "high T c superconductors", and will be referred to in that manner throughout the specification. This designation is meant to include both the materials having rare earth or rare earth-like elements in their crystalline structure, as well as the more recently reported materials which do not contain rare earth or rare earth-like elements. Generally, all these materials are copper oxide based superconductors having Cu-O planes that appear to be primarily responsible for carrying the supercurrents, where the copper oxide planes are separate or in groups separated by the ...

... [\*4] copper oxide material having a superconducting onset temperature greater than 77 K.

[\*5] 5. The device of claim 4, where said superconducting material includes an atom selected from the group consisting of rare earth atoms and rare earth-like atoms.

[\*6] 6. The device of claim 4, where said superconducting material includes an alkaline earth atoms.

[\*7] 7. The device of claim 4, where said superconducting material includes bismuth.

[\*8] 8. The device of claim 1, where ...  
 LEVEL 1 - 28 OF 68 PATENTS

&lt;=2&gt; GET 1st DRAWING SHEET OF 8

Nov. 3, 1992

## Zirconium-hafnium separation and purification process

INVENTOR: Ash, Kenneth C., Corvallis, Oregon  
 Crocker, William A., Salem, Oregon  
 Haygarth, John C., Corvallis, Oregon  
 Lee, David R., Lebanon, Oregon  
 Morris, Donald, Corvallis, Oregon  
 Peterson, John R., Salem, Oregon  
 Riesen, Jon A., Albany, Oregon  
 Yih, Robert S., Salem, Oregon

DETDISC:

... system or solution.

b) Sodium sulfate or any other source of soluble sulfate is then added in excess of the concentration of the barium plus radium ion equivalents and any other cations which might combine with the sulfate ions, i.e. calcium, rare earths, or the like. If the solution is cold, it should be heated and a digestion allowed to take place which can range from a fairly short time up to hours or days. The preferred digestion period would be a few hours with ...

LEVEL 1 - 29 OF 68 PATENTS

5,112,795

May 12, 1992

Supported silver catalyst, and processes for making and  
using same

INVENTOR: Minahan, David M., Cross Lanes, West Virginia  
Thorsteinson, Erlind M., Charleston, West Virginia  
Liu, Albert C., Charleston, West Virginia

SUM:

... metal promoter employed is not critical and may include the one or more alkali metals; one or more alkaline earth metals; or one or more other promoters, such as thallium, gold, tin, antimony, rare earths and the like. The catalysts produced are said to be equally as efficient as catalysts produced by coincidental methods of preparation.

Supported, silver-containing, alkylene oxide catalysts often include one or more metal- ...

LEVEL 1 - 30 OF 68 PATENTS

5,084,684

<=2> GET 1st DRAWING SHEET OF 5

Jan. 28, 1992

Method of adjusting a frequency response in a  
three-conductor type filter device

INVENTOR: Shimizu, Hiroyuki, Nagoya, Japan  
Ito, Kenji, Nagoya, Japan  
Wakita, Naomasa, Nagoya, Japan

SUM:

... each other. Each of the dielectric substrates 1 and 2 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 1 is provided with an external ground conducting layer 3 on the peripheral portion and bottom surface thereof. Similarly, the upper dielectric substrate 2 is provided with an external ground conducting layer 4 on the ...

DETDISC:

... assembling of the filter. Each of the dielectric substrates 11 and 12 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 11 is provided with a ground conducting layer 13 on the lower or outer surface thereof. Similarly, the upper dielectric substrate 12 is provided with a ground conducting layer 14 on the upper or ...

LEVEL 1 - 31 OF 68 PATENTS

5,084,312

A14



Jan. 28, 1992

Molten metal containment vessel with rare earth oxysulfide  
protective coating thereon and method of making same

INVENTOR: Krikorian, Oscar H., Danville, California  
Curtis, Paul G., Tracy, California

SUM:

... same. More particularly, this invention relates to an improved containment vessel for molten metals formed by coating at least the inside surface of a containment vessel with an oxysulfide or sulfide of a rare earth or rare earth-like element.

Molten metals such as uranium, plutonium, aluminum, and calcium are usually contained in vessels or crucibles made from graphite or a refractory metal such as, for example, niobium, tantalum, molybdenum, or tungsten. ...

... in which wetting of the vessel's surfaces by molten metal is inhibited by coating the surfaces of at least the inner walls of the containment vessel with one or more compounds comprising an oxysulfide of a rare earth or a rare earth-like element to inhibit such wetting and or adherence by the molten metal.

It is a further object of this invention to provide a method for making an improved molten metal containment vessel in which wetting of the surfaces by ...

DETDESC:

... rare earth oxysulfide or sulfide compound include the lanthanide elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; as well as the rare earth-like elements Sc and Y; and actinides such as Th and U. The term "rare earth" and "rare earth elements", as used herein, are therefore intended to define any of the above listed elements.

The rare earth oxysulfide and sulfide coatings of the ...  
LEVEL 1 - 32 OF 68 PATENTS

5,075,653

Dec. 24, 1991

Method of adjusting a frequency response in a  
three-conductor type filter device

INVENTOR: Ito, Kenji, Nagoya, Japan  
Shimizu, Hiroyuki, Nagoya, Japan

SUM:

... each other. Each of the dielectric substrates 1 and 2 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 1 is provided with an external ground conducting layer 3 on the peripheral portion and bottom surface thereof. Similarly, the upper dielectric substrate 2 is provided with an external ground conducting layer 4 on the ...

DETDESC:

... assembling of the filter. Each of the dielectric substrates 11 and 12 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 11 is provided with an external ground conducting layer 13 on the peripheral portion and outer surface thereof. Similarly, the upper dielectric substrate 12 is provided with an external ground conducting layer 14 on the ...

LEVEL 1 - 33 OF 68 PATENTS

&lt;=2&gt; GET 1st DRAWING SHEET OF 6

Nov. 19, 1991

## Method of adjusting a frequency response in a stripline filter device

INVENTOR: Ito, Kenji, Nagoya, Japan  
 Shimizu, Hiroyuki, Nagoya, Japan  
 Wakita, Naomasa, Nagoya, Japan

## SUM:

... each other. Each of the dielectric substrates 1 and 2 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 1 is provided with an external ground conducting layer 3 on the peripheral portion and bottom surface thereof. Similarly, the upper dielectric substrate 2 is provided with an external ground conducting layer 4 on the ...

## DETDISC:

... assembling of the filter. Each of the dielectric substrates 11 and 12 may be of dielectric ceramic material having a high dielectric constant and a lower dielectric loss such as BaO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>-rare earth or the like. The lower dielectric substrate 11 is provided with an external ground conducting layer 13 on the peripheral portion and outer surface thereof. Similarly, the upper dielectric substrate 12 is provided with an external ground conducting layer 14 on the ...

LEVEL 1 - 34 OF 68 PATENTS

5,045,289

&lt;=2&gt; GET 1st DRAWING SHEET OF 4

Sep. 3, 1991

## Formation of rare earth carbonates using supercritical carbon dioxide

INVENTOR: Fernando, Quintus, Tucson, Arizona  
 Yanagihara, Naohisa, Zacopan, New Mexico, Mexico  
 Dyke, James T., Santa Fe, New Mexico  
 Vemulapalli, Krishna, Tuscon, Arizona

## SUM:

... invention. This technique finds use in facilitating the extraction of these materials from rare earth containing mineral ores by providing a scheme for separating these particular rare earths from other rare earth and rare earth-like materials which do not react to form carbonates.

## 2. Description of the Prior Art

The rare earths, also known as the lanthanides or as lanthanons, and meaning here those elements having atomic numbers 57 to 71, are substances finding utility ...

## DETDISC:

... synthesis of rare earth carbonates from certain select rare earths in the trivalent (+3) state as normally found in, for example, rare earth oxides or hydroxides, from other rare earths or rare earth-like materials. Rare earth-like materials are those compounds associated with, normally present in, or formed during the processing of, the various source ores from which the lanthanides are derived. These materials, while not true rare earths are analogous to the lanthanides in structure and behavior and are therefore of concern during processing and separation. Included among these rare earth-like

materials are compounds formed from the actinides, (elements of atomic numbers 89 to 103, such as thorium), titanium, yttrium, and zirconium. In general, these elements, which form the rare earth-like compounds, are present in their + 4 oxidation state; examples include ThO<sub>2</sub> and ZrO<sub>2</sub>. The process of the invention has utility in the quantitative precipitation of the particular reactive lanthanides in the + 3 oxidation state and in the separation of these ...

... about 400 C. High yields of 95% or better are obtained in approximately one hour. These particular rare earth oxides or hydroxides can thus be readily separated from the oxides or hydroxides of rare earth or rare earth-like elements such as praseodymium (Pr), terbium (Tb), erbium (Er), ytterbium (Yb), zirconium (Zr), cerium (Ce), and thorium (Th) because these latter rare earth and rare earth-like oxides (or hydroxides) do not form carbonates under the above conditions despite the fact that some are in the trivalent state. It is believed that the oxides of these elements are particularly complex and as such do not readily react under the conditions of the invention.

This ...

Pat. No. 5045289, \*

... through appropriate valves and the reaction solution is then filtered. The solids which remain are then washed with deionized water and dried in air. These solids comprise both the rare earth materials which have reacted to form carbonates and also those rare earth and/or rare earth-like materials which did not react, or did not react significantly, and have thus remained in their oxide or hydroxide form.

The solid precipitate obtained above is next treated with a dilute acid such as HCl in a concentration of between 0.1 and 3.0M. Preferably 0.5M HCl is used at ambient temperature and pressure. This acid treatment solubilizes the rare earth carbonates, leaving the unreacted rare earth and rare earth-like oxides and/or hydroxides behind in their solid form. The resultant solution is filtered and the carbonate fraction can be further broken down into individual rare earth carbonates by techniques such as ion exchange or ...

... La<sub>2</sub>O<sub>3</sub>(49.72%), Nd<sub>2</sub>O<sub>3</sub>(20.02%), Tb<sub>4</sub>O<sub>7</sub>(5.08%), Yb<sub>2</sub>O<sub>3</sub>(5.10%) and ThO<sub>2</sub>(20.07%), a high degree of separation of La and Nd was obtained-namely, between 94.3% and 99.8%. Notably, the other rare earth or rare earth-like oxides in this mixture are among those which do not react to form carbonates with supercritical carbon dioxide or by the process of the invention.

The following example will illustrate and describe without limiting the invention. The example illustrates the carbonation process of the invention using essentially pure rare earth oxides.

#### EXAMPLE

#### Synthesis of Lanthanide Carbonates

The oxides of the following rare earths and rare earth-like materials, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Tb<sub>4</sub>O<sub>7</sub>, Dy<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>, were obtained from Alfa Division, Danvers, MA, and were 99.9% pure. The carbon dioxide used in this ...

LEVEL 1 - 35 OF 68 PATENTS

4,977,937

<=2> GET 1st DRAWING SHEET OF 4

Dec. 18, 1990

Multiple angle jointer and planer knives

INVENTOR: Hessenthaler, George D., 585 W. 3900 South, #6, Murray, Utah 84123

#### DETDESC:

... gibe or locking bars, not shown, are tightened, the blade magnets 53 are selected to attract even minimally magnetic material, such as carbide. To provide such magnetic attraction the selected magnets should be very strong,

A17

such as rare earth, or magnets.

Like the jointer jig 40, a planer jig 60, shown in FIGS. 9 and 10 also utilizes magnets for maintaining blade positioning in a cylindrical cutterhead 61 ...

PAG

LEVEL 1 - 36 OF 68 PATENTS

4,962,086

<=2> GET 1st DRAWING SHEET OF 2

Oct. 9, 1990

High T c superconductor - gallate crystal structures

INVENTOR: Gallagher, William J., Ardsley, New York  
Giess, Edward A., Purdys, New York  
Gupta, Aranova, Valley Cottage, New York  
Laibowitz, Robert B., Peekskill, New York  
O'Sullivan, Eugene J., Peekskill, New York  
Sandstrom, Robert L., Chappaqua, New York

ABST:

High T c oxide superconductive films can be formed on gallate layers, where the gallate layers include a rare earth element or a rare earth-like element. Combinations of rare earth elements and rare earth-like elements can also be utilized. The superconductive films can be epitaxially deposited on these gallate layers to form single crystals or, in the minimum, highly oriented superconductive layers. Any high T c superconductive ...

SUM:

... materials having Cu-O planes therein which are responsible for carrying supercurrents in these materials. Epitaxial films of these high T c superconductors can be deposited on gallate substrates, where the substrates are rare earth gallates or rare earth-like gallates. These superconductor-substrate combinations are particularly suited for analog and digital signal processing devices including matched filters, correlators, Fourier transformers, spectrum analyzers, samplers, A/D converters, etc.

...

... high T c superconductors.

The high T c superconductors used with these gallate substrates are preferably those which include Cu-O and Cu-O like current carrying planes and can include rare earth and rare earth-like elements, as well as combinations of these elements. Also included are the non-rare earth high T c superconductors such as those having Bi-Sr-Ca-Cu-O compositions and Tl-Ba-Ca-Cu- ...

... less than that when copper containing oxide superconductors are used. Lattice matching of the superconductor atomic spacing to the Ga-O plane is especially good with the copper oxide superconductors which form unique combinations with these gallates.

These rare earth and rare earth-like gallate substrates can be prepared in high quality crystal form and provide excellent lattice matches to the Cu-O based superconducting perovskites. This is important in device applications since for ...

DRWDESC:

BRIEF DESCRIPTION OF THE DRAWINGS

Pat. No. 4962086, \*

FIG. 1 illustrates a high T c superconducting film epitaxially deposited on a rare earth or rare earth-like gallate substrate.

FIG. 2 illustrates a structure including a high T c superconducting strip

line surrounded by a gallate lattice-matched insulator, further including high ...

DETDISC:

... 10 has been deposited on the crystal substrate 12. A cooling means, if needed, is not shown but is well known in the art.

Substrate 12 is a gallate substrate comprised of a rare earth or rare earth-like element, gallium, and oxygen. Examples include LaGaO<sub>3</sub> and NdGaO<sub>3</sub>. A mixed gallate can also be used, such as one prepared from La-Y solid solutions. This technique is used to provide different lattice ...

... for use in the substrate include elements 58-71 of the periodic table, and in particular, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The rare earth-like elements suitable for use in the gallate substrates include Y, La, Bi and Sc. As noted, combinations of these rare earth and rare earth-like elements can also be used.

For the copper oxide superconductors the rare earth elements Tb, Dy, Ho, Er, Tm, Yb, and Lu may not provide atomic spacings that give lattice ...

... one which in preferred form is characterized by Cu-O planes that are primarily responsible for carrying the supercurrents in these materials. They generally have a perovskite-related structure and can include rare earth and/or rare earth-like elements. These materials often include alkaline earth elements, as for example Ca, Ba, Sr, Mg, . . . An example of a 92o K. superconductor is the well known YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, which is the so-called " ...

... be difficult to stabilize the approximately 110o K. superconducting phase of Bi-Sr-Ca-Cu-O superconductors. However, a favorable epitaxial substrate chosen from the class of gallates including a rare earth or rare earth-like element may aid in stabilizing this and other high T<sub>c</sub> phases. A cut along the [110] orthorhombic unit cell of GdGaO<sub>3</sub> would expose a surface with a favorable lattice match which ...

... While the unit cell of this superconducting thin film is rotated 45o with respect to the unit cell of the perovskite substrate, such rotation will not be needed for epitaxial matches of different superconductors to the rare earth and rare earth-like gallate substrates. One of skill in the art would use an orientation of the substrate such that good epitaxy and lattice matching will occur with the chosen superconducting film. In this example, the a and b axes are in the plane of the ...

... approximates a (100) cubic perovskite surface. With this as a guide, the substrate boule material is cut to provide the desired orientation.

It has been noted that the gallate substrates including a rare earth element or a rare earth-like element exhibit good hardness and tolerance to high temperatures. However, it may be preferable to process the superconducting film at temperatures less than the rhombohedral-orthorhombic transition of the substrate in order to maintain the slight orthorhombicity of the substrate.

Pat. No. 4962086, \*

...

... Lett. 58, 2684 (1987).

In the practice of this invention, highly oriented films of high T<sub>c</sub> oxide superconductors have been deposited on gallate substrates. These substrates are those which include at least one rare earth element or rare earth-like element. The superconducting epitaxial films are highly oriented and can approximate single crystals.

In the further practice of this invention, these high T<sub>c</sub> oxide superconducting film-gallate substrate combinations are particularly suitable

...

... apparent to those of skill in the art that variations can be made therein without departing from the spirit and scope of the present invention. For example, the gallate substrate materials may include combinations of rare earth elements and rare earth-like elements, and may also be doped to slightly vary lattice parameters. Further, the superconductive films deposited on these substrates, while preferably being copper oxide-based superconductors, can include rare earth elements, rare earth-like elements, and alkaline earth elements. Still further, combinations of these elements may be present and, also, rare earth elements need not be present in the superconducting film.

The best epitaxial matches occur when the ...

LEVEL 1 - 37 OF 68 PATENTS

4,882,718

<=2> GET 1st DRAWING SHEET OF 3

Nov. 21, 1989

Single-head, direct overwrite magneto-optic system and method

INVENTOR: Kryder, Mark H., Pittsburgh, Pennsylvania  
Shieh, Han-Ping D., Pittsburgh, Pennsylvania

DETDISC:

... domain will realign and not grow. Ferrimagnetic alloys including light rare earths such as gadolinium usually provide good mobility but generally require an approximately equal proportion of a heavy rare earth like terbium to increase coercivity to an effective operating level.

A preferred formulation (in atomic %) tested in the laboratory is as follows:

Gd13 Tb13 Fe59 Co15 having a compensation temperature of 90o ...

LEVEL 1 - 38 OF 68 PATENTS

4,882,067

<=2> GET 1st DRAWING SHEET OF 1

Nov. 21, 1989

Process for the chemical bonding of heavy metals from sludge in the silicate structure of clays and shales and the manufacture of building and construction materials therewith

INVENTOR: Johnson, Barrett, Sunnyvale, California  
Rubenstein, Charles B., Los Gatos, California

DETDISC:

... containing heavy metals which are generally considered to be toxic to humans and animal life, including arsenic, cobalt, cadmium, chromium, lead, nickel, selenium, thallium, zinc, magnesium, copper, antimony, barium, molybdenum, rare earths and the like and incidental organic toxins. In general, the invented process comprises a batch or continuous operation for the processing of industrial waste and contaminated water. The process developed as described in this patent is not ...

LEVEL 1 - 39 OF 68 PATENTS

4,806,328

Feb. 21, 1989

Method of manufacturing monolithic glass members

INVENTOR: Van Lierop, Joseph G., Eindhoven, Netherlands  
Bogemann, Arnoldus B. M., Eindhoven, Netherlands

Felder, Willy J. B., Veldhoven, Netherlands  
Huizing, Albert, Eindhoven, Netherlands

SUM:

... example, to adjust the refractive index of the glass member obtained after densification of the gel at a given value and/or to control other physical properties. Examples of such compounds are alkoxy compounds of aluminium, titanium, boron, germanium, rare earths and the like, of which the alkoxy groups each generally do not comprise more than 4 carbon atoms. Nitrates, carbonates, acetates and other compounds which decompose easily while forming oxides, may optionally also be used. Fluorine ...

LEVEL 1 - 40 OF 68 PATENTS

4,775,820

<=2> GET 1st DRAWING SHEET OF 3

Oct. 4, 1988

Multilayer electroluminescent device

INVENTOR: Eguchi, Ken, Yokohama, Japan  
Kawada, Haruki, Kawasaki, Japan  
Nishimura, Yukuo, Sagamihara, Japan

SUM:

... composed of a material of EL function dispersed in a binder.

As the material of EL function, there have been known heretofore inorganic metal materials such as ZnS containing Mn, Cu, ReF<sub>3</sub> (Re: rare earths) or the like as an activating agent, and the like.

In the case of a thin film type EL device, the structure is suitable for the following purposes, that is, a thin luminescent layer can be formed so as to ...

LEVEL 1 - 41 OF 68 PATENTS

4,734,338

<=2> GET 1st DRAWING SHEET OF 3

Mar. 29, 1988

Electroluminescent device

INVENTOR: Eguchi, Ken, Yokohama, Japan  
Kawada, Haruki, Kawasaki, Japan  
Nishimura, Yukuo, Sagamihara, Japan

SUM:

... layer composed of a material of EL function dispersed in a binder.

As the material of EL function, there have been heretofore inorganic metal materials such as ZnS containing Mn, Cu, ReF<sub>3</sub> and (Re: rare earths) or the like as an activating agent, and the like.

In the case of a thin film type EL device, the structure is suitable for the following purposes, that is, a thin luminescent layer can be formed so as to ...

PAGE 46

LEVEL 1 - 42 OF 68 PATENTS

4,700,436

<=2> GET 1st DRAWING SHEET OF 4

Oct. 20, 1987

A21

INVENTOR: Morita, Tamao, 47-1, Arakawa 6-Chome, Arakawa-ku, Tokyo, Japan

SUM:

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the utilization of permanent magnets made of hard magnetic powder of ferrite, alnico, rare-earth and the like materials solidified with synthetic resin and then magnetized. More particularly, it relates to an improvement in magnetic material fastener means made of permanent magnet which is provided with magnetic plates at its magnetic poles.

2. Description of the Prior Art

...

LEVEL 1 - 43 OF 68 PATENTS

4,681,625

<=2> GET 1st DRAWING SHEET OF 11

Jul. 21, 1987

Methods for simultaneously desulfurizing and degassing  
steels

INVENTOR: Wilson, William G., 820 Harden Dr., Pittsburgh, Pennsylvania 15229

SUM:

... difficult to get into solution and also those whose recoveries from their addition have been less than the amount added to the steel such as electrolytic manganese, ferro-niobium, ferro-tungsten and the like. The metals that may be added include aluminum, calcium, barium, rare earths and the like. The recovery of elements in the steel from additions of metals and ferro-alloys is reduced in many cases in conventional steel making technology by their contact with slags high in oxides such as iron ...

... [\*21] metals to be added in the tube to enhance desulfurization are those which are known to have the ability to reduce the oxygen content of the steel, but also have the ability to form sulfides which would float out of the steel into the slag which include magnesium, calcium, barium, rare earths and the like.

[\*22] 22. The method as claimed in claims 1 or 5 wherein the ferro-alloys and elemental metals to be added in the tube are those necessary to obtain the desired chemical analysis of the finished steel such as ferro- ...

LEVEL 1 - 44 OF 68 PATENTS

4,598,914

<=2> GET 1st DRAWING SHEET OF 10

Jul. 8, 1986

Sealing and bearing means by use of ferrofluid

INVENTOR: Furumura, Kyozauro, Ninomiya, Japan  
Sugi, Hiromi, Fujisawa, Japan  
Murakami, Yasuo, Fujisawa, Japan  
Asai, Hiromitsu, Fujisawa, Japan

DETDISC:

... polyamide resin, fluorine resin, polyethersulfone resin, polyphenylene



sulfide resin or the like. The magnetic material to be used with the aforesaid synthetic resin material is made of barium ferrite powder, strontium ferrite powder, rare earths or the like.

The mixture ratio of the synthetic resin and the aforesaid normal magnetic substance is different in case the magnet is used for bearing purposes and sealing purposes.

In case the magnet is employed as bearing, it is to have enough ...

LEVEL 1 - 45 OF 68 PATENTS

4,582,688

<=2> GET 1st DRAWING SHEET OF 1

Apr. 15, 1986

Process for recovery of mineral values

INVENTOR: Venkatesan, Valadi N., Arlington, Texas

DETDESC:

... present, molybdenum can be selectively leached from the ore utilizing a leaching solution containing sodium bicarbonate and oxygen. Thus, for example, substances such as vanadium, molybdenum, selenium, nickel, copper, uranium, the rare earths and the like may be recovered using the process of the present invention. The main criteria is that at least one of the minerals found in the ore may be solubilized without the solubilization of at least one other mineral.

Thus, the present ...

... part of the uranium is present as a refractory uranium-mineral complex. For example, other minerals found in the form of a uranium-mineral complex, include copper, nickel, thorium, scandium, the rare earths, and the like.

Uranium minerals frequently occur in the highly siliceous rocks and sedimentary deposits, generally as a mixture of the insoluble tetravalent form and the soluble hexavalent form. Uranium is also found in association with the silicates, ...

LEVEL 1 - 46 OF 68 PATENTS

4,570,692

<=2> GET 1st DRAWING SHEET OF 6

Feb. 18, 1986

Methods of pouring metal

INVENTOR: Wilson, William G., 820 Harden Dr., Pittsburgh, Pennsylvania 15229

DETDESC:

... teeming operation and good distribution throughout the entire ingot can be expected. When the stability of the oxides in the slags is high, even the most reactive alloys such as aluminum, titanium, zirconium, magnesium, calcium or rare earths and the like will be transferred to the steel from the slag with maximum retention of the alloying element in the metal being teemed. The addition of these alloys along with these stable oxides that will not react with these alloying elements, the elimination of the flow ...

LEVEL 1 - 47 OF 68 PATENTS

4,491,563

Jan. 1, 1985

Process for deodorizing a paraffinic hydrocarbon feedstock

INVENTOR: Reusser, Robert., Bartlesville, Oklahoma  
Murtha, Timothy P., Bartlesville, Oklahoma  
Todd, Elizabeth A., Bartlesville, Oklahoma

DETDISC:

... examples are given to provide a better and more complete disclosure of this invention but should not be interpreted to limit its scope.

EXAMPLE I

This example describes a typical catalyst preparation whereby NiO and a rare earth like CeO is deposited on a support. This general procedure is also described in U.S. Pat. No. 4,217,248 column 7, line 49 to column 8, line 41. Two hundred grams of 13 x ...

LEVEL 1 - 48 OF 68 PATENTS

4,489,042

Dec. 18, 1984

Process for recovery of mineral values from subterranean formations

INVENTOR: Savins, Joseph G., Dallas, Texas  
Johnson, Warren F., Dallas, Texas

DETDISC:

... formations. However, it should be clear that the invention is applicable to the solution leaching of other mineral values capable of forming soluble reaction products with leaching solutions. Thus, for example, substances such as vanadium, molybdenum, nickel, copper, the rare earths and the like are recovered using the process of the present invention.

As an illustration, the leach chemistry of a uranium ore body can be described by the following equations using hydrogen peroxide (H2O2) as oxidant:

PAGE

LEVEL 1 - 49 OF 68 PATENTS

4,486,026

<=2> GET 1st DRAWING SHEET OF 10

Dec. 4, 1984

Sealing and bearing means by use of ferrofluid

INVENTOR: Furumura, Kyoaburo, Ninomiya, Japan  
Sugi, Hiromi, Fujisawa, Japan  
Murakami, Yasuo, Fujisawa, Japan  
Asai, Hiromitsu, Fujisawa, Japan

DETDISC:

... polyamide resin, fluorine resin, polyethersulfone resin, polyphenylene sulfide resin or the like. The magnetic material to be mixed with the aforesaid synthetic resin material is made of barium ferrite powder, strontium ferrite powder, rare earths or the like.

The mixture ratio of the synthetic resin and the aforesaid normal magnetic substance is different in case the magnet is used for bearing purposes and sealing purposes.

In case the magnet is employed as bearing, it is to have enough ...

PAGE 54

LEVEL 1 - 50 OF 68 PATENTS

4,481,437

A 24

Nov. 6, 1984

Variable flux permanent magnets electromagnetic machine

INVENTOR: Parker, Rollin J., Greenville, Michigan

DETDISC:

... cylindrical housing 12 in which is mounted, by any appropriate convenient means, a cylindrical tubular stator 14 comprising high strength permanent magnets such as ceramic, or ceramic rare earth, cobalt-rare earth, or the like [magents] magnets. Each one of a pair of end cap members 16 and 18 fastened at an end of the housing 12 by bolts or screws 20 supports respectively an end magnet ring 22 an ...

LEVEL 1 - 51 OF 68 PATENTS

4,455,392

Jun. 19, 1984

Process for preparing a supported silver catalyst

INVENTOR: Warner, Glenn H., St. Albans, West Virginia  
Bhasin, Madan M., Charleston, West Virginia  
Lieberman, Bernard, Kew Gardens, New York

SUM:

... as lithium, sodium, potassium, rubidium and/or cesium; one or more alkaline earth metals, such as, barium, magnesium and strontium; or one or more of the other known promoters, such as thallium, gold, tin, antimony and rare earths; and the like. For purposes of convenience, the catalyst preparation process of the invention is described below in terms of a silver-first method of preparation wherein the promoter is selected from among alkali metals, it being recognized that other promoters of ...

LEVEL 1 - 52 OF 68 PATENTS

4,438,077

Mar. 20, 1984

Two stage selective oxidative leach method to separately recover uranium and refractory uranium-mineral complexes

INVENTOR: Tsui, Tien-Fung, Richardson, Texas

SUM:

... least part of the uranium is present as a refractory uranium-mineral complex. For example, other minerals found in a uranium-mineral complex include copper, nickel, thorium, scandium, the rare earths, and the like.

Uranium minerals frequently occur in the highly siliceous rocks and sedimentary deposits, generally as a mixture of the insoluble tetravalent form and the soluble hexavalent form. Uranium is also found in association with the silicates, ...

LEVEL 1 - 53 OF 68 PATENTS

4,427,236

Jan. 24, 1984

In-situ uranium leaching

INVENTOR: Dotson, Billy J., Grand Prairie, Texas

DETDISC:

A25

... be clear that the invention is applicable to the solution mining of other mineral values capable of forming soluble reaction products with carbonated leaching solutions. Thus, for example, substances such as vanadium, molybdenum, nickel, copper, the rare earths and the like are recovered using the process of the present invention.

Uranium minerals frequently occur in the highly siliceous rocks and sedimentary deposits, generally as a mixture of the insoluble quadrivalent form and the soluble sexivalent form. ...

LEVEL 1 - 54 OF 68 PATENTS

4,419,276

Dec. 6, 1983

Silver catalyst for the manufacture of ethylene oxide and a process for preparing the catalyst

INVENTOR: Bhasin, Madan M., Charleston, West Virginia  
Warner, Glenn H., St. Albans, West Virginia

SUM:

... as lithium, sodium, potassium, rubidium and/or cesium; one or more alkaline earth metals, such as, barium, magnesium and strontium; or one or more of the other known promoters, such as thallium, gold, tin, antimony and rare earths; and the like. For purposes of convenience, the catalyst preparation process of the invention is described below in terms of a silver-first method of preparation wherein the promoter is selected from among alkali metals, it being recognized that other promoters of ...

PAGE 59

LEVEL 1 - 55 OF 68 PATENTS

4,405,380

Sep. 20, 1983

High strength, low alloy steel with improved surface and mechanical properties

INVENTOR: Griffith, Cecil B., North Royalton, Ohio  
Thomas, Jerry D., North Olmsted, Ohio  
Demianczuk, Dionisyj W., Parma, Ohio  
Abraham, John K., Broadview Heights, Ohio  
Franklin, Joseph E., Medina, Ohio

DETDESC:

... present invention is directed to a steel with carbon in the range of 0.03 to 0.06%, the last being an upper limit which also appears crucial for attainment of so-called auto-sulfide-shape control and thus avoidance of the use of rare earths or the like with their consequent expense and tendency to produce unwanted non-metallic surface inclusions.

The base metal may thus consist of the defined composition, with manganese in the range of 0.2 to 0.6%, very preferably not more than 0.45%, while the ...

PAGE 60

LEVEL 1 - 56 OF 68 PATENTS

4,376,264

<=2> GET 1st DRAWING SHEET OF 6

Mar. 8, 1983

Method of checking the authenticity of papers and physically identifiable paper for use in said method

A26

INVENTOR: Dokter, Hendr. D., Ugchelen, Netherlands  
Hilderling, Roelof, Frederikslaan, Netherlands  
Mackor, Adrianus, Hollandsche Rading, Netherlands

SUM:

... be some which show a suitable ESR spectrum, although to the knowledge of the present inventors this has never been investigated. However, a further requirement is that a useful ESR spectrum should be obtained at room temperature. Many compounds of rare earths and the like show a useful ESR spectrum only at low temperatures, such as the temperature of liquid nitrogen, but of course an identification of banknotes and the like is hardly of any practical value, if it cannot be carried out at normal room ...

PAGE 61

LEVEL 1 - 57 OF 68 PATENTS

4,367,163

<=2> GET 1st DRAWING SHEET OF 1

Jan. 4, 1983

Silica-clay complexes

INVENTOR: Pinnavaia, Thomas J., East Lansing, Michigan  
Mortland, Max M., East Lansing, Michigan  
Endo, Tadashi, East Lansing, Michigan

DETDESC:

... be used as a catalyst support for various catalytically active metals such as a Group VIII metal such as platinum, palladium, nickel, iron or cobalt; molybdenum; tungsten; a rare-earth and the like. Moreover, the intercalated product can be used in admixture with other common adsorbents or matrix materials such as silica, alumina, silica-alumina hydrogel and the like. The catalysts which can be prepared by ...

LEVEL 1 - 58 OF 68 PATENTS

4,358,158

<=2> GET 1st DRAWING SHEET OF 1

Nov. 9, 1982

Solution mining process

INVENTOR: Showalter, William E., Seal Beach, California

DETDESC:

... invention is applicable to the solution mining of other mineral values capable of forming soluble reaction products with the dilute carbonic acid leaching solution. Thus, for example, substances such as vanadium, molybdenum, nickel, copper, the rare earths and the like can be recovered using the process of the present invention.

Uranium minerals frequently occur in the highly siliceous rocks and sedimentary deposits, generally as a mixture of the insoluble quadrivalent form and the soluble ...

LEVEL 1 - 59 OF 68 PATENTS

4,358,157

<=2> GET 1st DRAWING SHEET OF 1

Nov. 9, 1982

Solution mining process

A27

INVENTOR: Showalter, William E., Seal Beach, California

DETDESC:

... invention is applicable to the solution mining of other mineral values capable of forming soluble reaction products with the dilute carbonic acid leaching solution. Thus, for example, substances such as vanadium, molybdenum, nickel, copper, the rare earths and the like can be recovered using the process of the present invention.

Uranium minerals frequently occur in the highly siliceous rocks and sedimentary deposits, generally as a mixture of the insoluble quadrivalent form and the soluble ...

LEVEL 1 - 60 OF 68 PATENTS

4,328,079

<=2> GET 1st DRAWING SHEET OF 1

May 4, 1982

Method for pumping impurities, especially noble gases, from hydrogen or mixtures of hydrogen and its isotopes

INVENTOR: Hemmerich, Johann, Stetternich, Federal Republic of Germany

DETDESC:

... 2 is adjusted by the fluid within the chamber 13 to the temperature for the desired hydrogen partial pressure. In this variation, the cathodes are formed from hydride-forming metals and alloys, for example, rare earth and rare earth-like metals and binary and ternary alloys of them with the addition of transition metals like iron, nickel, cobalt, etc. Upon formation of the sputtered film 12, hydrogen and its isotopes form hydrides with the film by chemisorption that can ...

LEVEL 1 - 61 OF 68 PATENTS

4,279,668

<=2> GET 1st DRAWING SHEET OF 7

Jul. 21, 1981

Directionally solidified ductile magnetic alloy

INVENTOR: Kurz, Wilfried, Lausanne, California, Switzerland  
Gardon, Remi, Berkeley, California

SUM:

... relates to a process for the fabrication of magnetic alloys for permanent magnets and to the magnetic bodies obtained by this process.

More particularly the invention relates to ternary magnetic alloys consisting of rare-earth or rare-earth-like elements, cobalt and at least one metal selected from the group which consists of iron, nickel, aluminum, copper, molybdenum or manganese. Preferably the latter metal phase includes 0.1 to 10% (atomic) of the total alloy as ...

LEVEL 1 - 62 OF 68 PATENTS

4,208,225

<=2> GET 1st DRAWING SHEET OF 6

Jun. 17, 1980

Directionally solidified ductile magnetic alloys  
magnetically hardened by precipitation hardening

INVENTOR: Kurz, Wilfried, Lausanne, Switzerland  
Glardon, Remi, Corseaux, Switzerland

SUM:

... relates to a process for the fabrication of magnetic alloys for permanent magnets and to the magnetic bodies obtained by this process.

More particularly the invention relates to ternary magnetic alloys consisting of rare-earth or rare earth-like elements, cobalt and at least one metal selected from the group which consists of iron, nickel, aluminum, copper, molybdenum or manganese.

BACKGROUND OF THE INVENTION

Ferromagnetic alloys of the cobalt/rare-earth type have a high energy ...

LEVEL 1 - 63 OF 68 PATENTS

4,105,253

<=2> GET 1st DRAWING SHEET OF 1

Aug. 8, 1978

Process for recovery of mineral values from underground  
formations

INVENTOR: Showalter, William E., Seal Beach, California

DETDESC:

... be clear that the invention is applicable to the solution mining of other mineral values capable of forming soluble reaction products with carbonated leaching solutions. Thus, for example, substances such as vanadium, molybdenum, nickel, copper, the rare earths and the like are recovered using the process of the present invention.

Uranium minerals frequently occur in the highly siliceous rocks and sedimentary deposits, generally as a mixture of the insoluble quadrivalent form and the soluble sexivalent form. ...

LEVEL 1 - 64 OF 68 PATENTS

4,050,052

<=2> GET 1st DRAWING SHEET OF 1

Sep. 20, 1977

Electrical temperature measuring resistor structure,  
particularly for resistance thermometers

INVENTOR: Reichelt, Walter, Hanau, Germany, Federal Republic of  
Sauer, Gunter, Maintal, Germany, Federal Republic of

DETDESC:

... temperatures can be applied. This cover layer, shown in FIG. 2 schematically at 3, may consist for example of an epoxy resin, glass, or metal oxides of the group of aluminum, beryllium, thorium, rare earths, or the like. The cover layer 3 may be applied by vapor deposition, dusting, or spraying; its primary characteristics should be to be resistant against thermal and mechanical effects. The cover layer should additionally, preferably, provide ...

LEVEL 1 - 65 OF 68 PATENTS

4,014,706

Mar. 29, 1977

Solid solution ceramic materials

INVENTOR: Waldron, Robert D., Scottsdale, Arizona

SUM:

... dimensions of said structure and all physical and chemical properties of the solution are continuous functions of composition. The lattice symmetry may change within said composition range by uniform distortion of the structure as the composition changes.

Rare earth-like (metallic) elements as used herein means elements of atomic numbers 21, 39, and/or 57-71.

Yttrium earth (metallic) elements as used herein means elements of atomic numbers 39 and/or 64-71.

...

PAGE

LEVEL 1 - 66 OF 68 PATENTS

3,983,077

<=2> GET 1st DRAWING SHEET OF 2

Sep. 28, 1976

Process for making ceramic resistor materials

INVENTOR: Fuller, Peter G., Lakeville, Massachusetts  
Stoeckler, Hans A., Woonsocket, Rhode Island

DETDESC:

... invention also typically include additions of silicon oxide or manganese oxide or the like and other dopants typically incorporated in such ceramic compositions include lanthanum, cerium, dysprosium, and praesodymium as well as other rare earths and the like commonly used in ceramic resistor materials of positive temperature coefficient of resistivity. Typically, the ceramic titanate materials produced by the process are provided with stoichiometric or slightly titanium-rich compositions, the compositions preferably having an ...

LEVEL 1 - 67 OF 68 PATENTS

3,896,616

<=2> GET 1st DRAWING SHEET OF 1

Jul. 29, 1975

Process and apparatus

INVENTOR: Keith, Carl D., Summit, New Jersey  
Mooney, John J., Wyckoff, New Jersey

DETDESC:

... 0.1 to 1.5%. The catalytic element may contain, with or without the platinum group metals, one or more catalytic materials which may include, for example, chromium, manganese, vanadium, copper, iron, cobalt, nickel, rare earths, and the like.

The relative sizes of the initial and subsequent catalytic elements may be such that their volume ratio, i.e. the superficial volume of the subsequent catalyst to the initial catalyst, including void spaces within the catalytic masses, is often at least about ...

LEVEL 1 - 68 OF 68 PATENTS

3,791,143

<=2> GET 1st DRAWING SHEET OF 1

Feb. 12, 1974

PROCESS AND APPARATUS

A 30



INVENTOR: Keith, Carl D., Summit, New Jersey  
Mooney, John J., Wyckoff, New Jersey

DETDESC:

... 1.5 percent. The catalytic element may contain, with or without the platinum group metals, one or more catalytic materials which may include, for example, chromium, manganese, vanadium, copper, iron, cobalt, nickel, rare earths, and the like.

The relative sizes of the initial and subsequent catalytic elements may be such that their volume ratio, i.e., the superficial volume of the subsequent catalyst to the initial catalyst, including void spaces within the catalytic masses, is often at least about ...

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|---|-------------------|-----------------|-----------|--------|---|
| * | 72 PAGES          | 1431 LINES      | JOB 97027 | 100G6J | * |
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Attachment B

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Mon, 24 Nov 1997 12:52:15 -0500  
Message-Id: <199711241752.AA13241@prod.lexis-nexis.com>  
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Mon, 24 Nov 1997 12:52:15 -0500  
Date: Mon, 24 Nov 97 12:52:14 EST  
From: lexis-nexis@prod.lexis-nexis.com (LEXIS(R)/NEXIS(R) Print Delivery)  
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\*\*\*\*\*03404\*\*\*\*\*

LEVEL 1 - 1 OF 4 PATENTS

5,344,815

<=2> GET 1st DRAWING SHEET OF 4

Sep. 6, 1994

Fabrication of high T C superconducting helical resonator  
coils

INVENTOR: Su, Sophia R., Weston, Massachusetts  
O'Connor, Margaret, Worcester, Massachusetts  
Butler, Scott, N. Oxford, Massachusetts

... [\*13] oxygen for at least 2 hr.

[\*14] 14. A method in accordance with claim 11 wherein said mixture further  
comprises at least about 3 w/o grain aligned clusters of a like rare earth  
barium copper oxide superconductor.

[\*15] 15. A method in accordance with claim 11 wherein said rare earth

barium copper oxide superconductor is an yttrium barium copper oxide superconductor.

[\*16] 16. A ...

LEVEL 1 - 2 OF 4 PATENTS

5,236,091

<=2> GET 1st DRAWING SHEET OF 5

Aug. 17, 1993

Eddy current separator and method of making a rotor

INVENTOR: Kauppila, Raymond, Marquette, Michigan  
Nowak, Gregory, Girard, Pennsylvania

... as follows:

[\*1] 1. A rotor for an eddy current separator comprising a rotor body having generally cylindrical, outer peripheral surfaces designed to be rotated at a design speed;

plate-like rare earth permanent magnets;

adhesive means attaching said plate-like rare earth permanent magnets to said outer peripheral surfaces of said rotor body at a bond line;

said plate-like rare earth permanent magnets being disposed in longitudinal rows extending from one end of said rotor to the other;

said plate-like rare earth permanent magnets in a particular row having a polarity on their outer end opposite the polarity of an outer end of said plate-like permanent magnets in adjacent rows;

a fiber means ...

... [\*3] equal to that of carbon.

[\*4] 4. A rotor for an eddy current separator comprising a rotor body having generally cylindrical, outer peripheral surfaces designed to be rotated at a design speed;

plate-like rare earth permanent magnets;

adhesive means attaching said plate-like rare earth permanent magnets to said outer peripheral surfaces of said rotor body at a bond line;

said plate-like rare earth permanent magnets being disposed in longitudinal rows extending from one end of said rotor to the other;

said plate-like rare earth permanent magnets in a particular row having a polarity on their outer end opposite the polarity of an outer end of said plate-like permanent magnets in adjacent rows;

fiber means wrapped ...

... [\*7] body having a polygonal outer periphery;

said polygonal outer periphery having a plurality of circumferentially disposed adjacent flat surfaces of equal width extending longitudinally of  
Pat. No. 5236091, \*7

said rotor from end to end thereof;

plate-like rare earth permanent magnets having a width substantially equal to the width of sides of said polygonal outer periphery and attached to said flat

surfaces by adhesive;

said plate-like rare earth permanent magnets extending substantially continuously from end to end of said rotor;

said shell being made of an electrically non-conductive material and adapted to receive said rotor;

a heat shield being ...

LEVEL 1 - 3 OF 4 PATENTS

5,162,298

<=2> GET 1st DRAWING SHEET OF 5

Nov. 10, 1992

Grain boundary junction devices using high T c  
superconductors

INVENTOR: Chaudhari, Praveen, Briarcliff Manor, New York  
Chi, Cheng-Chung J., Yorktown Heights, New York  
Dimos, Duane B., Upper Montclair, New Jersey  
Mannhart, Jochen D., Metzingen, New York, Federal Republic of Germany  
Tsuei, Chang C., Chappaqua, New York

... [\*4] copper oxide material having a superconducting onset temperature greater than 77 K.

[\*5] 5. The device of claim 4, where said superconducting material includes an atom selected from the group consisting of rare earth atoms and rare earth-like atoms.

[\*6] 6. The device of claim 4, where said superconducting material includes an alkaline earth atoms.

[\*7] 7. The device of claim 4, where said superconducting material includes bismuth.

[\*8] 8. The device of claim 1, where ...

LEVEL 1 - 4 OF 4 PATENTS

4,681,625

<=2> GET 1st DRAWING SHEET OF 11

Jul. 21, 1987

Methods for simultaneously desulfurizing and degassing  
steels

INVENTOR: Wilson, William G., 820 Harden Dr., Pittsburgh, Pennsylvania 15229

... [\*21] metals to be added in the tube to enhance desulfurization are those which are known to have the ability to reduce the oxygen content of the steel, but also have the ability to form sulfides which would float out of the steel into the slag which include magnesium, calcium, barium, rare earths and the like.

[\*22] 22. The method as claimed in claims 1 or 5 wherein the ferro-alloys and elemental metals to be added in the tube are those necessary to obtain the desired chemical analysis of the finished steel such as ferro- ...

\* 5 PAGES

99 LINES

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Attachment C

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Sat, 22 Nov 1997 17:36:59 -0500  
Date: Sat, 22 Nov 97 17:36:58 EST  
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To: dmorris@watson.ibm.com  
Subject: LEXIS(R)/NEXIS(R) Print Request Job 97085, 1 of 2

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NUMBER OF PATENTS FOUND WITH YOUR FOCUS REQUEST:  
107

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\*\*\*\*\*06089\*\*\*\*\*  
FOCUS - 1 OF 107 PATENTS

5,686,394

<=2> GET 1st DRAWING SHEET OF 1

Nov. 11, 1997

Process for manufacturing a superconducting composite

INVENTOR: Sibata, Kenichiro, Hyogo, Japan  
Sasaki, Nobuyuki, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

SUM:

... Ho-Cu-O system or Ba-Dy-Cu-O system compound oxide which possess the  
quasi-perovskite type crystal structure including an orthorhombically distorted  
perovskite or a distorted oxygen-deficient perovskite or the like.

The abovementioned type superconductors can be prepared from a powder mixture consisting of oxides and/or carbonates containing constituent elements of said superconductor. The powder mixture may include optionally oxides and/or carbonates of at least ...

FOCUS - 2 OF 107 PATENTS

5,679,980

<=2> GET 1st DRAWING SHEET OF 5

Oct. 21, 1997

Conductive exotic-nitride barrier layer for  
high-dielectric-constant material electrodes

INVENTOR: Summerfelt, Scott R., Dallas, Texas

DETDESC:

...  
TABLE

\*

\*

Conductive perovskite like

FOCUS - 3 OF 107 PATENTS

5,665,628

<=2> GET 1st DRAWING SHEET OF 5

Sep. 9, 1997

Method of forming conductive amorphous-nitride barrier layer  
for high-dielectric-constant material electrodes

INVENTOR: Summerfelt, Scott R., Dallas, Texas

DETDESC:

...  
TABLE

\*

\*

Conductive perovskite like

FOCUS - 4 OF 107 PATENTS

5,661,112

<=2> GET 1st DRAWING SHEET OF 3

Aug. 26, 1997

Superconductor

INVENTOR: Hatta, Shinichiro, 201-1028, Higashinakafuri-2-chome, Hirakata-shi, Japan

Higashino, Hidetaka, A2-505, 117, Hitotsuyacho, Matsubara-shi, Japan

Hirochi, Kumiko, 22, Keihanondori-1-chome, Moriguchi-shi, Japan

Adachi, Hideaki, 3-1-505, Mitsuiminamimachi, Neyagawa-shi, Japan

... [\*1] film being a transition metal element selected from Pt, Au, Ag, Pd, Ni and Ti the composition A-B-Cu-O of said oxide film being in the form of layered perovskite-like structure.

[\*2] 2. A superconductor according to claim 1, wherein an additional metal film is formed on said oxide film, or the oxide films and metal films are laminated alternately to form a multi-layer structure.

[\*3] ...

FOCUS - 5 OF 107 PATENTS



&lt;=2&gt; GET 1st DRAWING SHEET OF 4

Jul. 15, 1997

Chemical vapor deposition process for fabricating layered  
superlattice materials

INVENTOR: Paz De Araujo, Carlos A., Colorado Springs, Colorado  
 Watanabe, Hitoshi, Tokyo, Japan  
 Scott, Michael C., Colorado Springs, Colorado  
 Mihara, Takashi, Saitama, Japan

## DETDISC:

... Layered superlattice materials may be summarized more generally under the formula: [See Original Patent for Chemical Structure Diagram]

where A1, A2 . . . A represent A-site elements in the perovskite-like structure, which may be elements such as strontium, calcium, barium, bismuth, lead, and others, S1, S2 . . . Sk represent super-lattice generator elements, which usually is bismuth, but can also be materials such as yttrium, scandium, lanthanum, antimony, chromium, thallium, and other elements with a valence of + 3, B1, B2 . . . B1 represent B-site elements in the perovskite-like structure, which may be elements such as titanium, tantalum, hafnium, tungsten, niobium, zirconium, and other elements, and Q represents an anion, which may be elements such as oxygen, fluorine, chlorine and hybrids of these elements, such ...

... [\*14]  $s_2 > \dots S_k[x_k] < + s_k > B_1[y_1] < + b_1 > B_2[y_2] < + b_2 > \dots$   
 $B_1[y_1] < + b_1 > Q[z] < - 2 >$ , where A1, A2 . . . Aj represent A-site elements in a perovskite-like structure, S1, S2 . . . Sk represent superlattice generator elements, B1, B2 . . . B1 represent B-site elements in said perovskite-like structure, Q represents an anion, the superscripts indicate valences of the respective elements, the subscripts indicate an average number of atoms of the element in the unit cell, and at least w1 and y1 are non-zero, and wherein said  
 A- ... PAG

FOCUS - 6 OF 107 PATENTS

5,647,904

&lt;=2&gt; GET 1st DRAWING SHEET OF 2

Jul. 15, 1997

Method for manufacturing superconducting ceramics in a  
magnetic field

INVENTOR: Yamazaki, Shunpei, Tokyo, Japan

## SUM:

... 300 K. by a method in which a mixture of chemicals in a suitable composition is compacted and fired. These superconducting ceramics form a quasi-molecular atomic unit in a perovskite-like structure whose unit cell is constructed with one layer in which electrons have essentially one-dimensional motion, whereas a number of crystalline grains are arranged at random with diverse crystalline directions, and therefore the critical current density is

...

... cm from conventional several millimeters. The breadth and thickness may be more flexibly controlled by skilled persons according to the invention in comparison with the prior art technique.

Superconducting materials are constructed in perovskite-like structures as illustrated in FIG. 1 in accordance with the present invention. The structure comprises copper atoms 2, an intervening copper atom 3, oxygen atoms 5 and 6 surrounding the copper ...

DRWDESC:  
BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing the configuration of the perovskite-like molecular structure in accordance with the present invention.

FIGS. 2(A) and 2(B) are top and side sectional views showing an apparatus for manufacturing superconducting ceramics in accordance with the present invention.

FOCUS - 7 OF 107 PATENTS

5,646,094

<=2> GET 1st DRAWING SHEET OF 4

Jul. 8, 1997

Rare earth substituted thallium-based superconductors

INVENTOR: Tallon, Jeffrey Lewis, 3 Marine Drive, York Bay, Eastbourne, New Zealand  
Presland, Murray Robert, 4/1 Mahina Bay Road, Mahina Bay, Eastbourne, New Zealand

ABST:

... lanthanide rare earth elements and where  $0.3 \leq a, b \leq 0.7$ ,  $0.05 \leq c \leq 1.1$ ,  $2 - c \leq d \leq 1.95$ ,  $0.05 \leq e \leq 1$ ,  $1.9 \leq f \leq 2.1$  and  $6.5 \leq g \leq 7.5$ . These compounds, which are layered perovskite-like oxides, exhibit a high chemical stability, form readily into nearly single phase, do not require adjustment of oxygen stoichiometry after synthesis and compositions may be chosen allowing superconductivity at temperatures ...

SUM:

... for example, do not require adjustment of oxygen stoichiometry after synthesis, and compositions may be chosen allowing superconductivity at temperatures exceeding 100 K.

The novel compounds described herein have the same tetragonal layered perovskite-like structure of the parent compound  $Tl_{0.5}Pb_{0.5}CaSr_2Cu_{207}$  comprising in sequence: a  $Tl_{0.5}Pb_{0.5}O$  layer with Tl/Pb occupying square corner-shared sites and oxygen distributed about the face centre; a SrO layer with ...

FOCUS - 8 OF 107 PATENTS

5,626,906

<=2> GET 1st DRAWING SHEET OF 3

May 6, 1997

Electrodes comprising conductive perovskite-seed layers for perovskite dielectrics

INVENTOR: Summerfelt, Scott R., Dallas, Texas  
Beratan, Howard R., Dallas, Texas

ABST:

... layer and the conductive oxide layer each comprise the same metal. The metal should be conductive in its metallic state and should remain conductive when partially or fully oxidized. Generally, the perovskite-seed layer has a perovskite or perovskite-like crystal structure and lattice parameters which are similar to the perovskite dielectric layer formed thereon. At a given deposition temperature, the crystal quality and other properties of the perovskite dielectric will generally be enhanced by depositing it on ...

SUM:

... As used herein, the term "high-dielectric-constant" means a dielectric constant greater than about 50 at device operating temperature. As used herein the term "perovskite" means a material with a perovskite or perovskite-like

crystal structure. As used herein the term "dielectric", when used in reference to a perovskite, means a non-conductive perovskite, pyroelectric, ferroelectric, or high-dielectric-constant oxide material. The deposition of a ...

... structure. To facilitate perovskite crystal formation, perovskite dielectrics such as PZT have been deposited on some conductive perovskites such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $(\text{La}, \text{Sr})\text{CoO}_3$ . Deposition of PZT on a substrate with a perovskite or perovskite-like crystal structure normally minimizes the formation of the pyrochlore phase and improves the properties of the perovskite dielectric. However, the materials used thus far for the deposition surface have several problems. For example, they typically involve new cations such ...

... layer each comprise the same metal. The metal should be conductive in its metallic state and should remain conductive when partially or fully oxidized, and when in a perovskite. Generally, the perovskite-seed layer has a perovskite or perovskite-like crystal structure and lattice parameters which are similar to the perovskite dielectric layer formed thereon. At a given deposition temperature, the crystal quality and other properties of the perovskite dielectric will generally be enhanced by depositing it on ...

DETDISC:

TABLE

ruthenate      seed layer      perovskite-like materials  
FOCUS - 9 OF 107 PATENTS

5,611,854

Mar. 18, 1997

Seed crystals with improved properties for melt processing  
superconductors for practical applications

INVENTOR: Veal, Boyd W., Downers Grove, Illinois  
Paulikas, Arvydas, Downers Grove, Illinois  
Balachandran, Uthamalingam, Hinsdale, Illinois  
Zhong, Wei, Chicago, Illinois

DETDISC:

... Although  $\text{PbTiO}_3$  is shown in the Table, other perovskites of the form  $\text{RTiO}_3$ , when R is La or a rare earth are good candidates.  $\text{EuTiO}_3$  has a lattice parameter of 3,897 [Angstrom].  $\text{NdGaO}_3$ , and other perovskite-like oxides with the prototype  $\text{GdFeO}_3$  structure should also serve well.  $\text{NdGaO}_3$  is available as a commercial substrate material. Others may also be commercially available, particularly  $\text{LaCrO}_3$  which has many industrial applications.

Oxides with the  $\text{GdFeO}_3$  ( ...  
FOCUS - 10 OF 107 PATENTS

5,602,080

<=2> GET 1st DRAWING SHEET OF 1

Feb. 11, 1997

Method for manufacturing lattice-matched substrates for  
high-T<sub>c</sub> superconductor films

INVENTOR: Bednorz, Johannes G., Wolfhausen, Switzerland  
Mannhart, Jochen D., Thalwil, Switzerland  
Mueller, Carl A., Hedingen, Switzerland  
Schlom, Darrell G., State College, Pennsylvania

SUM:

... a close match-preferably approaching an ideal match-of the lattice parameters of a substrate-without a buffer layer-to a selected high-T<sub>c</sub>

]superconductor material having a perovskite or a perovskite-like crystal structure can be achieved by a method comprising the following steps:  
Determining the relevant lattice constant or constants of the selected superconductor material; choosing a desired orientation of the superconductor layer to ...

... for the deposition of the superconductor.

One preferred method of the invention for manufacturing a lattice-matched substrate for a film of a selected high-T<sub>c</sub> superconductor material having a perovskite or perovskite-like crystal structure at a selected orientation relative to the film dimensions comprises the steps set forth below.

The preferred method of the invention includes the step of determining a relevant lattice constant or constants of the selected ...

... make the codeposition from separate sources each containing one or more of the materials combined to form the buffer layer.

Preferred substrate component materials include strontium titanate SrTiO<sub>3</sub> and lanthanum aluminate LaAlO<sub>3</sub> for perovskite-like superconductor materials such as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> -  $\delta$ .

In the following description, a preferred method for manufacturing crystalline substrate material having essentially the same lattice constant as the corresponding lattice constant of a ...

FOCUS - 11 OF 107 PATENTS

5,593,951

<=2> GET 1st DRAWING SHEET OF 4

Jan. 14, 1997

Epitaxy of high T<sub>c</sub> superconductors on silicon

INVENTOR: Himpel, Franz J., Mt. Kisco, New York

SUM:

... first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure.

Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O system have been found to exhibit a superconducting transition temperature in excess of 77K. R. B. ...

FOCUS - 12 OF 107 PATENTS

5,590,053

<=2> GET 1st DRAWING SHEET OF 20

Dec. 31, 1996

Method of determining a space group

INVENTOR: Ito, Tatsuya, Kawasaki, Japan  
Kawai, Masahito, Kawasaki, Japan  
Yasukawa, Yoshihito, Kawasaki, Japan

DETDISC:

... present invention will be described with reference to FIG. 15 to FIG. 20. Let it be assumed here that a crystal as a target of analysis is one of LaGdSrCuO<sub>4</sub>. In the case of investigation into such a perovskite-like copper oxide superconductor, it is an effective technique of investigating a new substance to laminate partial structures to grasp a laminate structure

characteristic of the substance. The structure analysis of the target crystal by this technique will ...

FOCUS - 13 OF 107 PATENTS

5,589,284

<=2> GET 1st DRAWING SHEET OF 3

Dec. 31, 1996

Electrodes comprising conductive perovskite-seed layers for perovskite dielectrics

INVENTOR: Summerfelt, Scott R., Dallas, Texas  
Beratan, Howard R., Dallas, Texas

ABST:

... layer and the conductive oxide layer each comprise the same metal. The metal should be conductive in its metallic state and should remain conductive when partially or fully oxidized. Generally, the perovskite-seed layer has a perovskite or perovskite-like crystal structure and lattice parameters which are similar to the perovskite dielectric layer formed thereon. At a given deposition temperature, the crystal quality and other properties of the perovskite dielectric will generally be enhanced by depositing it on ...

SUM:

... As used herein, the term "high-dielectric-constant" means a dielectric constant greater than about 50 at device operating temperature. As used herein the term "perovskite" means a material with a perovskite or perovskite-like crystal structure. As used herein the term "dielectric", when used in reference to a perovskite, means a non-conductive perovskite, pyroelectric, ferroelectric, or high-dielectric-constant oxide material. The deposition of a ...

... structure. To facilitate perovskite crystal formation, perovskite dielectrics such as PZT have been deposited on some conductive perovskite such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $(\text{La}, \text{Sr})\text{CoO}_3$ . Deposition of PZT on a substrate with a perovskite or perovskite-like crystal structure normally minimizes the formation of the pyrochlore phase and improves the properties of the perovskite dielectric. However, the materials used thus far for the deposition surface have several problems. For example, they typically involve new cations such ...

... layer each comprise the same metal. The metal should be conductive in its metallic state and should remain conductive when partially or fully oxidized, and when in a perovskite. Generally, the perovskite-seed layer has a perovskite or perovskite-like crystal structure and lattice parameters which are similar to the perovskite dielectric layer formed thereon. At a given deposition temperature, the crystal quality and other properties of the perovskite dielectric will generally be enhanced by depositing it on ...

DETDISC:

...  
TABLE  
...

ruthenate  
\*

seed layer  
\*

perovskites or perovskite-  
like materials (e.g.

FOCUS - 14 OF 107 PATENTS

5,585,300

<=2> GET 1st DRAWING SHEET OF 5

Dec. 17, 1996

Method of making conductive amorphous-nitride barrier layer for high-dielectric-constant material electrodes

INVENTOR: Summerfelt, Scott R., Dallas, Texas

DETDESC:

...  
TABLE

\*

\*

...  
Conductive perovskite like  
FOCUS - 15 OF 107 PATENTS

5,583,096

<=2> GET 1st DRAWING SHEET OF 8

Dec. 10, 1996

Superconductive compounds and process for producing said  
compounds

INVENTOR: Cavazos, Ramon G., Paseo de la Reforma 403, Primer Piso, Mexico D.F.  
06500

DETDESC:

... A. Muller in their article entitled "Possible High Tc Superconductivity in Ba-La-Cu-O System". (Zeitschrift fur Physik B-Condensed Matter 64,189-193 (1986), reported: "... perovskite-like-mixed valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally, an abrupt decrease by ...

FOCUS - 16 OF 107 PATENTS

5,563,331

<=2> GET 1st DRAWING SHEET OF 3

Oct. 8, 1996

Magnetoresistive sensor utilizing a sensor material with a  
perovskite-like crystal structure

INVENTOR: Von Helmholt, Rittmar, Erlangen, Federal Republic of Germany  
Wecker, Joachim, Roettenbach, Federal Republic of Germany

ABST:

A magnetoresistive sensor may be constructed with material having a perovskite-like crystal structure and an increased magnetoresistive effect. The material is based on the composition  $(A1)[1-x](A2)[x]MnO[z]$ , with A1 (trivalent) selected from Y, La, or a lanthanide, A2 (bivalent) from an alkaline- ...

SUM:

BACKGROUND OF THE INVENTION

The present invention relates to a magnetoresistive sensor with a layer made of a sensor material that possesses a perovskite-like crystal structure and exhibits an increased magnetoresistive effect.

The general structure and operation of magnetoresistive sensors with thin films made of ferromagnetic transition metals are explained further in, for example, the book "Sensors", Vol. ...

...  $x]Se$  (cf. "Journal of Applied Physics," Vol. 38, No. 3, Mar. 1, 1967, pp. 959-964). A corresponding effect is also evident in  $Nd_{0.5}Pb_{0.5}MnO_3$  crystals; these crystals have a perovskite-like structure (cf. "Physics B," Vol. 155, 1989, pp. 362-365). However, the change in electrical resistance as a function of magnetic induction observed in these material systems is confined to low ...

... occur only to a reduced extent, in a sensor material that is the subject of a German patent application No. P 43 10 318.9 (not previously disclosed).

This material possesses a perovskite-like crystal structure and exhibits an increased magnetoresistive effect. A composition based on  $(A1)[1-x](A2)[x]MnO[x]$  is to be selected for the material, such that the trivalent constituent A1 at least contains ...

... sensor according to an embodiment of the present invention includes at least two layers, a first layer and a second layer. Each of the first and second layers is made of a sensor material that possesses a perovskite-like crystal structure and exhibits an increased magnetoresistive effect. The sensor material of each of the first and second layers has a composition based on  $(A1)[1-x](A2)[x]MnO[z]$ , where A1 is a trivalent ...

DETDESC:

... indicated can also contain minimal impurities with less than 0.5 atomic percent of each impurity element. Exemplary embodiments for corresponding materials are therefore  $La_{0.67}Ba_{0.33}MnO_3$ , or  $Pr_{0.5}Sr_{0.5}MnO_3$ , or  $Nd_{0.33}Ca_{0.67}MnO_3$ , or  $(Dy_{0.67}Mg_{0.33})(Mn_{0.8}Cu_{0.2})O_{2.9}$ . All these materials have  
Pat. No. 5563331, \*

FOCUS

a perovskite-like crystal structure and are characterized by an increased magnetoresistive effect  $M[r]$  of, in particular, more than 10%, and preferably more than 50%. The effect is thus considerably greater than in known Cu/Co multilayer systems.

...

... 1557-1559). According to the present invention, corresponding layers of the sensor material are advantageously deposited onto substrates whose respective crystalline unit cell has dimensions matched to the unit cell of the sensor material. Substrate materials that also have a perovskite-like crystal structure are therefore particularly suitable. Corresponding exemplary embodiments are  $SrTiO_3$ ,  $MgO$ ,  $LaAlO_3$ ,  $NdGaO_3$ ,  $MgAl_2O_4$ , or Y-stabilized  $ZrO_2$  (abbreviated YSZ). In addition, however, Si substrates that are coated with a special intermediate ...

... [\*1] a layer system comprising at least two layers, including:

a first layer; and

a second layer;

wherein each of said first and second layers comprises a sensor material that possesses a perovskite-like crystal structure and exhibits an increased magnetoresistive effect, such that the sensor material of each of said first and second layers has a composition based on  $(A1)[1-x](A2)[x]MnO[z]$ , wherein A1 is a ...

... [\*4] similar to said first layer and layers similar to said second layer.

[\*5] 5. A magnetoresistive sensor according to claim 2; wherein the layer system is deposited on a substrate made of a material that has a perovskite-like crystal structure.

[\*6] 6. A magnetoresistive sensor according to claim 1, wherein the first layer and the second layer have different thicknesses.

[\*7] 7. A magnetoresistive sensor according to claim 6, wherein the layer system includes ...

... [\*7] similar to said first layer and layers similar to said second layer.

[\*8] 8. A magnetoresistive sensor according to claim 6, wherein the layer system is deposited on a substrate made of a material that has a perovskite-like crystal structure.

[\*9] 9. A magnetoresistive sensor according to claim 1, wherein the layer system includes more than two layers which alternate between layers similar to said first layer and layers similar to said second layer.

[\*10] 10. A magnetoresistive sensor according to claim 9, wherein the layer system is deposited on a substrate made of a material that has a  
Pat. No. 5563331, \*10

FOCUS

perovskite-like crystal structure.

[\*11] 11. A magnetoresistive sensor according to claim 1, wherein the layer system is deposited on a substrate made of a material that has a perovskite-like crystal structure.

[\*12] 12. A magnetoresistive sensor according to claim 1, wherein  $0.25 \leq x \leq 0.75$ .

[\*13] 13. A magnetoresistive sensor according to claim 1, wherein  $z = 3$ .  
FOCUS - 17 OF 107 PATENTS

5,554,585

<=2> GET 1st DRAWING SHEET OF 1

Sep. 10, 1996

Method of forming a superconductor microstrip transmission  
line

INVENTOR: Simon, Randy W., Long Beach, California  
Platt, Christine E., El Segundo, California  
Lee, Alfred E., Torrance, California  
Lee, Gregory S., West Los Angeles, California

REF-CITED:

... 61(1):28-35 (1973).  
Geballe, "Paths to Higher Temperature Superconductors," Science, vol. 259, Mar. 12, 1993, pp. 1550-1551.  
Geller, S., et al., "Crystallographic Studies of Perovskite-like Compounds. II. Rare Earth Aluminates," Acta. Cryst., 9:1019-1025 (1956).  
Geller, S., "Crystallographic Studies of Perovskite-like Compounds. IV. Rare Earth Scandates, Vanadites, Galliates, Orthochromites," Acta Cryst., 10:243-248 (1957).  
Gulyaev, Yu V., et al., "YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Films with a High-temperature ...  
FOCUS - 18 OF 107 PATENTS

5,552,373

<=2> GET 1st DRAWING SHEET OF 2

Sep. 3, 1996

Josephson junction device comprising high critical  
temperature crystalline copper superconductive layers

INVENTOR: Agostinelli, John A., Rochester, New York  
Mir, Jose M., Webster, New York  
Lubberts, Gerrit, Penfield, New York  
Chen, Samuel, Penfield, New York

DETDISC:

... can take any convenient form capable of permitting deposition of USCO" thereon as a thin film.

In a specifically preferred form of the invention SUB" is chosen from



materials that themselves exhibit a perovskite or perovskite-like crystal structure. Strontium titanate is an example of a perovskite crystal structure which is specifically preferred for use as a substrate. Lanthanum aluminate ( $\text{LaAlO}_3$ ), lanthanum gallium oxide ( $\text{LaGaO}_3$ ) and potassium tantalate are ...

FOCUS - 19 OF 107 PATENTS

5,527,567

<=2> GET 1st DRAWING SHEET OF 6

Jun. 18, 1996

Metalorganic chemical vapor deposition of layered structure  
oxides

INVENTOR: Desu, Seshu B., Blacksburg, Virginia  
Tao, Wei, Blacksburg, Virginia  
Peng, Chien H., Blacksburg, Virginia  
Li, Tingkai, Blacksburg, Virginia  
Zhu, Yongfei, Blacksburg, Virginia

SUM:

... 1961), 695; G. A. Smolenski, V. A. Isupov and A. I. Agranovskaya, Fiz Tverdogo Tela, 3, (1961), 895). These compounds have a pseudo-tetragonal symmetry and the structure is comprised of stacking of perovskite-like units between ( $\text{Bi}_2\text{O}_2$ )<sup>2+</sup> layers along the pseudo-tetragonal c-axis. A large number of these compounds do not contain any volatile components in their sublattice that exhibits spontaneous polarization. The tendency for ...

PAGE 22

FOCUS - 20 OF 107 PATENTS

5,523,283

<=2> GET 1st DRAWING SHEET OF 1

Jun. 4, 1996

$\text{L[a]AlO}_3$  Substrate for copper oxide superconductors

INVENTOR: Simon, Randy W., Long Beach, California  
Platt, Christine E., El Segundo, California  
Lee, Alfred E., Torrance, California  
Lee, Gregory S., West Los Angeles, California

REF-CITED:

... 61(1):28-35 (1973).  
Gaballe, "Paths to Higher Temperature Superconductors," Science, vol. 259, Mar. 12, 1993, pp. 1550-1551.  
Geller, S., et al., "Crystallographic Studies of Perovskite-like Compounds. II. Rare Earth Aluminates," Acta. Cryst., 9:1019-1025 (1956).  
Geller, S., "Crystallographic Studies of Perovskite-like Compounds. IV. Rare Earth Scandates, Vanadites, Galliates, Orthochromites," Acta Cryst., 10:243-428 (1957).  
Gulysev, Yu V., et al., " $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Films with a High-temperature ...

FOCUS - 21 OF 107 PATENTS

5,523,282

<=2> GET 1st DRAWING SHEET OF 1

Jun. 4, 1996

High-frequency substrate material for thin-film layered  
perovskite superconductors

INVENTOR: Simon, Randy W., Long Beach, California

C11

Platt, Christine E., El Segundo, California  
Lee, Alfred E., Torrance, California  
Lee, Gregory S., West Los Angeles, California

REF-CITED:

... A., et al., "The Flux Shuttle-A Josephson Junction Shift Register Employing Single Flux Quanta," Proceedings of the IEEE, 61(1):28-35 (1973).  
Geller, S., "Crystallographic Studies of Perovskite-like Compounds. Rare Earth Scandates, Vanadites, Galliates, Orthochromites," Acta Cryst., 10:243-251 (1957).  
Gurvitch, M., et al., "Preparation and Substrate Reactions of Superconducting Y-Ba-Cu-O Films," ...

... in the Coprecipitation of Carbonate and Hydroxide Compounds of Lanthanum and Aluminum," Russian Journal of Inorganic Chemistry, vol. 22, No. 11, pp. 1622-1625, 1977.

S. Geller et al., "Crystallographic Studies of Perovskite-like Compounds. II. Rare Earth Aluminates," Acta Cryst., vol. 9, pp. 1019-1025, 1956.

J. Kilner et al., "Electrolytes for the High Temperature Fuel Cell; Experimental and Theoretical ...

FOCUS - 22 OF 107 PATENTS

5,519,234

<=2> GET 1st DRAWING SHEET OF 30

May 21, 1996

Ferroelectric dielectric memory cell can switch at least  
giga cycles and has low fatigue - has high dielectric  
constant and low leakage current

INVENTOR: Paz de Araujo, Carlos A., Colorado Springs, Colorado  
Cuchiario, Joseph D., Colorado Springs, Colorado  
Scott, Michael C., Colorado Springs, Colorado  
McMillan, Larry D., Colorado Springs, Colorado

ABST:

...  $s_2 > \dots S_k x_k < + a_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_l y_l < + b_l > Q z < - 2 >$ , where  $A_1, A_2 \dots A_j$  represent A-site elements in a perovskite-like structure,  $S_1, S_2 \dots S_k$  represent superlattice generator elements,  $B_1, B_2 \dots B_l$  represent B-site elements in a perovskite-like structure,  $Q$  represents an anion, the superscripts indicate the valences of the respective elements, the subscripts indicate the number of atoms of the element in the unit cell, and at least  $w_1$  and  $y_1$  are non-zero. Some of these materials are extremely low ...

SUM:

... 676 (1962) and Chapter 8 pages 241-292 and pages 624 & 625 of Appendix F of the Lines and Glass reference cited above. As outlined in section 15.3 of the Smolenskii book, the layered perovskite-like materials can be classified under three general types:

(I) compounds having the formula  $A_{m-1}Bi_2M_mO_{3m+3}$ , where  $A = Bi_{<3+>}$ ,  $Ba_{<2+>}$ ,  $Sr_{< >}$  ...

... strontium titanates  $Sr_2TiO_4$ ,  $Sr_3Ti_2O_7$  and  $Sr_4Ti_3O_{10}$ ; and

(III) compounds having the formula  $A_mM_mO_{3m+2}$ , including compounds such as  $Sr_2Nb_2O_7$ ,  $La_2Ti_2O_7$ ,  $Sr_5TiNb_4O_{17}$ , and  $Sr_6Ti_2Nb_4O_{20}$ .

Smolenskii pointed out that the perovskite-like layers may have different thicknesses, depending on the value of  $m$ , and that the perovskite  $AMO_3$  is in principal the limiting example of any type of layered perovskite-like structure with  $m = \text{infinity}$ . Smolenskii also noted that if the layer with minimum thickness ( $m = 1$ ) is denoted by  $P$  and the bismuth-oxygen layer is denoted by  $B$ , then the type I compounds may be described as ...  $BP_m BP_m \dots$ . Further

Smolenskii noted that if  $i$  is a fractional number then the lattice contains perovskite-like layers of various thicknesses, and that all the known type I compounds are ferroelectrics. Similarly, Smolenskii noted that the type two compounds could be represented as  $\dots SP_m SP_m \dots$  where P is the perovskite-like layer of thickness m and S is the strontium-oxygen connecting layer, and that since the type I and type II compounds have similar perovskite-like layers, the existence of "hybrid" compounds such as  $\dots BP_m SP_n BP_m SP_m \dots$  "should not be ruled out", though none had been obtained at that time.

Pat. No. 5519234, \*

FOCUS

Up to now, these layered ferroelectric ...

$\dots s_2 > \dots S_k x_k < + s_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_1 y_1 < + b_1 > Q z < - 2 >$ , where  $A_1, A_2 \dots A_j$  represent A-site elements in a perovskite-like structure,  $S_1, S_2 \dots S_k$  represent superlattice generator elements,  $B_1, B_2 \dots B_l$  represent B-site elements in a perovskite-like structure, Q represents an anion, the superscripts indicate the valences of the respective elements, the subscripts indicate the average number of atoms of the element in the unit cell, and at least  $w_1$  and  $y_1$  are non-zero. Preferably, the A- ...

... layered superlattice material comprises a material having a localized structure, within a grain or other larger or smaller unit, which localized structure contains predominately repeatable units containing one or more perovskite-like layers and one or more intermediate non-perovskite-like layers spontaneously linked in an interdependent manner.

In another aspect the invention provides a non-volatile ferroelectric memory comprising: a ferroelectric memory cell including a layered superlattice ...

DETDESC:

... curves as shown in FIG. 5C, which show fatigue of less than 30%, which is much less than for any ferroelectric material on which endurance tests had been performed in the prior art. It was realized that the  $SrBi_4Ti_4O_{15}$  was one of the layered perovskite-like materials catalogued by Smolenskii, and thought that perhaps the natural layered structure of these materials might be the source of the low-fatigue property. Other devices were fabricated having the structure shown in FIG. 2C, i.e. a ...

... flexible than the lattice of a ferroelectric material. Turning to FIG. 13, a layered superlattice material 92 is illustrated. Smolenskii recognized that what we call the layered superlattice materials spontaneously form into layers 94 with a perovskite-like structure which alternate with layers 96 having a simpler structure. Depending on the material, the perovskite-like layers 94 may include one or a plurality of linked layers of perovskite-like octahedrons 90. As an example, FIG. 14 shows a unit cell of the material  $ABi_2B_2 < + 5 > O_9$ , which is the formula for strontium bismuth tantalate ( $SrBi_2Ta_2O_9$ ) and other layered superlattice materials, such as tantalum, niobium, and tungsten, having an element with a valence of + 5 in the B-site. In this structure, each perovskite-like layer 94 includes two layers of octahedrons 90 which are separated by layers 96 of a material that does not have a perovskite-like structure. In this material the primitive unit cell consists of two perovskite layers 94 and two non-perovskite layers 96, since the structure shifts between the layers 98A and 98B. In FIG. ...

...  $O_{15}$ , which is the formula for strontium bismuth titanate ( $SrBi_4Ti_4O_{15}$ ) and other layered superlattice materials having an element, such as titanium, hafnium, and zirconium, having a valence of + 4 in the B-sites. In this material each the perovskite-like layer 94 has four layers of octahedrons 90.

As the understanding of what Smolenskii called a layered perovskite-like structure increased, the inventors have realized that these materials are more than a substance which spontaneously forms in layers. This is seen most easily by an example. Strontium bismuth tantalate ( $SrBi_2Ta_2O_9$ ) can be considered to

Pat. No. 5519234, \*

be ...

... in the following definition: (B) a material having a localized structure, within a grain or other larger or smaller unit, which localized structure contains predominately repeatable units containing one or more perovskite-like layers and one or more intermediate non-perovskite-like layers spontaneously linked in an interdependent manner.

It has been discovered that the layered superlattice materials catalogued by Smolenskii et al. are all likely candidates for fatigue free switching ferroelectrics and dielectric materials that are resistant to ...

...  $x_2 < + s_2 > \dots S_k x_k < + s_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_l y_l < + b_l > Q z < - 2 >$  ,

where  $A_1, A_2 \dots A_j$  represent A-site elements in the perovskite-like structure, which may be elements such as strontium, calcium, barium, bismuth, lead, and others  $S_1, S_2 \dots S_k$  represent superlattice generator elements, which usually is bismuth, but can also be materials such as yttrium, scandium, lanthanum, antimony, chromium, thallium, and other elements with a valence of +3,  $B_1, B_2 \dots B_l$  represent B-site elements in the perovskite-like structure, which may be elements such as titanium, tantalum, hafnium, tungsten, niobium, zirconium, and other elements, and Q represents an anion, which generally is oxygen but may also be other elements, such as fluorine, ...

... [\*2]  $s_2 > \dots S_k x_k < + s_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_l y_l < + b_l > Q z < - 2 >$  , where  $A_1, A_2 \dots A_j$  represent A-site elements in a perovskite-like structure,  $S_1, S_2 \dots S_k$  represent superlattice generator elements,  $B_1, B_2 \dots B_l$  represent B-site elements in a perovskite-like structure, Q represents an anion, the superscripts indicate the valences of the respective elements, the subscripts indicate the average number of atoms of the element in the unit cell, and at least  $w_1$  and  $y_1$  are non-zero.

[\*3] 3. A ...

FOCUS - 23 OF 107 PATENTS

5,504,041

<=2> GET 1st DRAWING SHEET OF 5

Apr. 2, 1996

Conductive exotic-nitride barrier layer for  
high-dielectric-constant materials

INVENTOR: Summerfelt, Scott R., Dallas, Texas

DETDESC:

...  
TABLE

\*

\*

...  
Conductive perovskite like materials  
FOCUS - 24 OF 107 PATENTS

5,489,548

<=2> GET 1st DRAWING SHEET OF 3

Feb. 6, 1996

Method of forming high-dielectric-constant material  
electrodes comprising sidewall spacers

INVENTOR: Nishioka, Yasushiro, Tsukuba, Texas, Japan  
Summerfelt, Scott R., Dallas, Texas

Park, Kyung-Ho, Tsukuba, Japan  
Bhattacharya, Pijush, Midnapur, India

DETDISC:

TABLE

\* \* Conductive perovskite like  
FOCUS - 25 OF 107 PATENTS

5,478,610

<=2> GET 1st DRAWING SHEET OF 5

Dec. 26, 1995

Metalorganic chemical vapor deposition of layered structure  
oxides

INVENTOR: Desu, Seshu B., Blacksburg, Virginia  
Tao, W., Blacksburg, Virginia

SUM:

... 34, (1961), 695; G. A. Smolenski, V. A. Isupov and A. I. Agranovskaya, Fiz Tverdogo Tela, 3, (1961), 895). These compounds have pseudo-tetragonal symmetry and the structure is comprised of stacking of perovskite-like units between  $(\text{Bi}_2\text{O}_2)^{2+}$  layers along the pseudo-tetragonal c-axis. A large number of these compounds do not contain any volatile components in their sublattice that exhibits spontaneous polarization. The tendency for ...

FOCUS - 26 OF 107 PATENTS

5,468,679

<=2> GET 1st DRAWING SHEET OF 27

Nov. 21, 1995

Process for fabricating materials for ferroelectric, high  
dielectric constant, and integrated circuit applications

INVENTOR: Paz de Araujo, Carlos A., Colorado Springs, Colorado  
Scott, Michael C., Colorado Springs, Colorado  
Cuchiaro, Joseph D., Colorado Springs, Colorado  
McMillan, Larry D., Colorado Springs, Colorado

SUM:

... 676 (1962) and Chapter 8 pages 241-292 and pages 624 & 625 of Appendix F of the Lines and Glass reference cited above.

As outlined in section 15.3 of the Smolenskii book, the layered perovskite-like materials can be classified under three general types:

(I) compounds having the formula  $A_{m-1}\text{Bi}_2\text{M}_m\text{O}_{3m+3}$ , where  $A = \text{Bi}_{3+}$ ,  $\text{Ba}_{2+}$ ,  $\text{Sr}_{2+}$  ...

...  $s_2 > \dots S_k x_k < + s_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_l y_l < + b_l > Q$   
 $z < - 2 >$ ,

where  $A_1, A_2 \dots A_j$  represent A-site elements in a perovskite-like structure,  $S_1, S_2 \dots S_k$  represent superlattice generator elements,  $B_1, B_2 \dots B_l$  represent B-site elements in a perovskite-like structure, Q represents an anion, the superscripts indicate the valences of the respective elements, the subscripts indicate the average number of atoms of the element in the unit cell, and at least  $w_1$  and  $y_1$  are non-zero. Preferably, the A- ...

DETDISC:

... compatible with, or can be designed to be compatible with, the other

materials commonly used, integrated circuits, such as silicon and gallium arsenide.

The class of materials are those disclosed by Smolenskii as having a layered perovskite-like structure, as discussed in the Background of the Invention. It has been realized that these materials are more than a substance which spontaneously forms in layers. This is seen most easily by an example. Strontium bismuth tantalate ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ) can ...

... in the following definition: (B) a material having a localized structure, within a grain or other larger or smaller unit, which localized structure contains predominately repeatable units containing one or more perovskite-like layers and one or more intermediate non-perovskite-like layers spontaneously linked in an interdependent manner.

It is well-known that compounds having the perovskite structure may be described in terms of the general formula  $\text{ABQ}_3$ , where A and B are cations and Q is an anion. In the ...

Pat. No. 5468679, \*

FOCUS

... flexible than the lattice of a ferroelectric material. Turning to FIG. 13, a layered superlattice material 92 is illustrated. Smolenskii recognized that what we call the layered superlattice materials spontaneously form into layers 94 with a perovskite-like structure which alternate with layers 96 having a simpler structure. Depending on the material, the perovskite-like layers 94 may include one or a plurality of linked layers of perovskite-like octahedrons 90. As an example, FIG. 14 shows a unit cell of the material  $\text{ABi}_2\text{B}_2\text{O}_9$ , which is the formula for strontium bismuth tantalate ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ) and other layered superlattice materials, such as tantalum, niobium, and tungsten, having a element with a valence of + 5 in the B-site. In this structure, each perovskite-like layer 94 includes two layers of octahedrons 90 which are separated by layers 96 of a material that does not have a perovskite-like structure. In this material the primitive unit cell consists of two perovskite layers 94 and two non-perovskite layers 96, since the structure shifts between the layers 98A and 98B. In FIG. ...

... 015, which is the formula for strontium bismuth titanate ( $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ) and other layered superlattice materials having an element, such as titanium, hafnium, and zirconium, having a valence of + 4 in the B-sites. In this material each the perovskite-like layer 94 has four layers of octahedrons 90.

It has been discovered that the layered superlattice materials catalogued by Smolenskii et al. are all likely candidates for fatigue free switching ferroelectrics and dielectric materials that are resistant to ...

...  $x_2 < + s_2 > \dots S_k x_k < + s_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_l y_l < b_l > Q z < - 2 >$ ,

where  $A_1, A_2 \dots A_j$  represent A-site elements in the perovskite-like structure, which may be elements such as strontium, calcium, barium, bismuth, lead, and others  $S_1, S_2 \dots S_k$  represent superlattice generator elements, which usually is bismuth, but can also be materials such as yttrium, scandium, lanthanum, antimony, chromium, thallium, and other elements with a valence of + 3,  $B_1, B_2 \dots B_l$  represent B-site elements in the perovskite-like structure, which may be elements such as titanium, tantalum, hafnium, tungsten, niobium, zirconium, and other elements, and Q represents an anion, which generally is oxygen but may also be other elements, such as fluorine, ...

FOCUS - 27 OF 107 PATENTS

5,447,908

<=2> GET 1st DRAWING SHEET OF 1

Sep. 5, 1995

Superconducting thin film and a method for preparing the

C16

same

INVENTOR: Itozaki, Hideo, Hyogo, Japan  
Tanaka, Saburo, Hyogo, Japan  
Fujita, Nobuhiko, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

SUM:

... structure. The term of quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to Perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygendeficient perovskite or the like.

The superconducting thin film may be also another type of superconductor consisting mainly of a compound oxide represented by the formula:

THETA 4( PHI 1-q ,Ca q ) m Cu ...

FOCUS - 28 OF 107 PATENTS

5,447,906

Sep. 5, 1995

Thin film high TC oxide superconductors and vapor deposition  
methods for making the same

INVENTOR: Chaudhari, Praveen, Briarcliff Manor, New York  
Gambino, Richard J., Yorktown Heights, New York  
Koch, Roger H., Amawalk, New York  
Lacey, James A., Mahopac, New York  
Laibowitz, Robert B., Peekskill, New York  
Viggiano, Joseph M., Wappingers Falls, New York

SUM:

... areas.

It is another object of the present invention to provide continuous, smooth copper oxide superconductive films exhibiting superconductivity at temperatures in excess of 40o K. and methods for making these films, where the films exhibit perovskite-like structure.

It is another object of this invention to provide transition metal oxide superconductive films including a rare earth element, or rare earth-like element, where the films exhibit superconductivity at temperatures greater than 40o ...

... earth-like element, B is an alkaline earth element, and y is sufficient to satisfy valence demands of the composition.

It is another object of the present invention to provide smooth, continuous copper oxide superconducting films having a perovskite-like crystal structure and exhibiting superconductivity at temperatures in excess of 40o K., and to provide methods for making these films.

#### SUMMARY OF THE INVENTION

The films of this invention are oxide superconductors exhibiting superconductivity at temperatures in excess of ...

... addition to being continuous, smooth, and of excellent compositional uniformity. The Cu oxide films are therefore considered to be unique examples of this class of films, as are the processes for making them.

Typically, the films are characterized by a perovskite-like crystalline structure, such as those described in more detail by C. Michel and B. Rayeau in Revue Dde.

5,439,878

<=2> GET 1st DRAWING SHEET OF 21

Aug. 8, 1995

Method for preparing copper oxide superconductor containing  
carbonate radicals

INVENTOR: Kinoshita, Kyoichi, Hoya, Japan  
Yamada, Tomoaki, Higashimurayama, Japan

SUM:

... novel superconducting material.  
Description of the Prior Art

Several types of copper oxide superconductors have been discovered since high-T<sub>c</sub> superconductivity was detected in the La-Ba-Cu-O system. Superconductivity would arise from the layered perovskite-like structure having CuO<sub>6</sub> octahedra, or CuO<sub>5</sub> pyramids, or CuO<sub>2</sub> square planes as a building unit. The layered perovskite-like structure and a sufficient carrier concentration of the material are essential factors for making the material superconducting as indicated by Osamura & Zhang (Japan. J. Appl. Phys. 26, L2094-L2096, 1987). ...

FOCUS - 30 OF 107 PATENTS

5,439,876

<=2> GET 1st DRAWING SHEET OF 5

Aug. 8, 1995

Method of making artificial layered high T<sub>c</sub> superconductors

INVENTOR: Graf, Volker, Wollerau, Switzerland  
Mueller, Carl A., Hedingen, Switzerland

DETDESC:

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

One material particularly suited as a substrate in the epitaxial growth of high T<sub>c</sub> superconductor material is strontium titanate, SrTiO<sub>3</sub>, which forms crystals like perovskite (FIG. 1). Each titanium ion 1 is octahedrally surrounded by six oxygen ions 2, the bigger strontium ions 3 being disposed in the spaces in between. At room temperature, ...

FOCUS - 31 OF 107 PATENTS

5,426,092

<=2> GET 1st DRAWING SHEET OF 14

Jun. 20, 1995

Continuous or semi-continuous laser ablation method for depositing fluorinated superconducting thin film having basal plane alignment of the unit cells deposited on non-lattice-matched substrates

INVENTOR: Ovshinsky, Stanford R., Bloomfield Hills, Michigan  
Young, Rosa, Troy, Michigan

SUM:

... growth of a crystalline superconducting material in a manner as if mimicking the orientation of a substrate having an identical lattice structure



without the presence of a substrate lattice structure. Simply stated, an "epitaxial-like" perovskite superconducting material grown on a non-lattice-matched substrate would nonetheless be characterized by a lattice structure identical to the lattice structure which would be present if the material was grown on a perovskite substrate. Thus, "...

FOCUS - 32 OF 107 PATENTS

5,424,282

<=2> GET 1st DRAWING SHEET OF 5

Jun. 13, 1995

Process for manufacturing a composite oxide superconducting wire

INVENTOR: Yamamoto, Susumu, Hyogo, Japan  
Murai, Teruyuki, Hyogo, Japan  
Kawabe, Nozomu, Hyogo, Japan  
Awazu, Tomoyuki, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

DETDISC:

... term of "quasiperovskite type structure" means any oxide that can be considered to have such a crystal structure that is similar to perovskite-type oxides and may include an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

In practice, the element alpha is preferably selected from Ba, Sr and/or Ca and the element beta is preferably selected from Y, La and/or lanthanid such as Sc, Ce, Gd, Ho, Er, Tin, Y b, ...

FOCUS - 33 OF 107 PATENTS

5,423,285

<=2> GET 1st DRAWING SHEET OF 27

Jun. 13, 1995

Process for fabricating materials for ferroelectric, high dielectric constant, and integrated circuit applications

INVENTOR: Paz de Araujo, Carlos A., Colorado Springs, Colorado  
Cuchiaro, Joseph D., Colorado Springs, Colorado  
Scott, Michael C., Colorado Springs, Colorado  
McMillan, Larry D., Colorado Springs, Colorado

SUM:

... 676 (1962) and Chapter 8 pages 241-292 and pages 624 & 625 of Appendix F of the Lines and Glass reference cited above.

As outlined in section 15.3 of the Smolenskii book, the layered perovskite-like materials can be classified under three general types:

(I) compounds having the formula  $A_{m-1}Bi_2M_mO_{3m+3}$ , where  $A = Bi_{<3+>}$ ,  $Ba_{<2+>}$ ,  $Sr_{<...>}$

...  $s_2 > \dots S_k x_k < + s_k > B_1 y_1 < + b_1 > B_2 y_2 < + b_2 > \dots B_l y_l < + b_l > Q$   
 $z < - 2 >$ , where  $A_1, A_2 \dots A_j$  represent A-site elements in a perovskite-like structure,  $S_1, S_2 \dots S_k$  represent superlattice generator elements,  $B_1, B_2 \dots B_l$  represent B-site elements in a perovskite-like structure,  $Q$  represents an anion, the superscripts indicate the valences of the respective elements, the subscripts indicate the average number of atoms of the element in the unit cell, and at least  $w_1$  and  $y_1$  are non-zero. Preferably, the A- ...

DETDISC:

... compatible with, can be designed to be compatible with, the other materials commonly used in integrated circuits, such as silicon and gallium arsenide.

The class of materials are those disclosed by Smolenskii as having a layered perovskite-like structure, as discussed in the Background of the Invention. It has been realized that these materials are more than a substance which spontaneously forms in layers. This is seen most easily by an example. Strontium bismuth tantalate ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ) can ...

... in the following definition: (B) a material having a localized structure, within a grain or other larger or smaller unit, which localized structure contains predominately repeatable units containing one or more perovskite-like layers and one or more intermediate non-perovskite-like layers spontaneously linked in an interdependent manner.

It is well-known that compounds having the perovskite structure may be described in terms of the general formula  $\text{ABQ}_3$ , where A and B are cations and Q is an anion. In the ...

... flexible than the lattice of a ferroelectric material. Turning to FIG. 13, a layered superlattice material 92 is illustrated. Smolenskii recognized Pat. No. 5423285, \*

FOCUS

that what we call the layered superlattice materials spontaneously form into layers 94 with a perovskite-like structure which alternate with layers 96 having a simpler structure. Depending on the material, the perovskite-like layers 94 may include one or a plurality of linked layers of perovskite-like octahedrons 90. As an example, FIG. 14 shows a unit cell of the material  $\text{ABi}_2\text{B}_2\text{O}_9$ , which is the formula for strontium bismuth tantalate ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ) and other layered superlattice materials, such as tantalum, niobium, and tungsten, having a element with a valence of + 5 in the B-site. In this structure, each perovskite-like layer 94 includes two layers of octahedrons 90 which are separated by layers 96 of a material that does not have a perovskite-like structure. In this material the primitive unit cell consists of two perovskite layers 94 and two non-perovskite layers 96, since the structure shifts between the layers 98A and 98B. in FIG. ...

... 015, which is the formula for strontium bismuth titanate ( $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ) and other layered superlattice materials having an element, such as titanium, hafnium, and zirconium, having a valence of + 4 in the B-sites. In this material each the perovskite-like layer 94 has four layers of octahedrons 90.

It has been discovered that the layered superlattice materials catalogued by Smolenskii et al. are all likely candidates for fatigue free switching ferroelectrics and dielectric materials that are resistant to ...

...  $\text{Sk xk} < + \text{sk} > \text{B1 y1} < + \text{b1} > \text{B2 y2} < + \text{b2} > \dots \text{B1 y1} < + \text{b1} > \text{Q z} < - 2 >$   
,tm (1)

where  $\text{A1}, \text{A2} \dots \text{Aj}$  represent A-site elements in the perovskite-like structure, which may be elements such as strontium, calcium, barium, bismuth, lead, and others  $\text{S1}, \text{S2} \dots \text{Sk}$  represent superlattice generator elements, which usually is bismuth, but can also be materials such as yttrium, scandium, lanthanum, antimony, chromium, thallium, and other elements with a valence of + 3,  $\text{B1}, \text{B2} \dots \text{B1}$  represent B-site elements in the perovskite-like structure, which may be elements such as titanium, tantalum, hafnium, tungsten, niobium, zirconium, and other elements, and Q represents an anion, which generally is oxygen but may also be other elements, such as fluorine, ...

FOCUS - 34 OF 107 PATENTS

5,409,890

Apr. 25, 1995

Process for producing an elongated sintered article

INVENTOR: Yamamoto, Susumu, Hyogo, Japan  
Kawabe, Nozomu, Hyogo, Japan  
Awazu, Tomoyuki, Hyogo, Japan  
Murai, Teruyuki, Hyogo, Japan

SUM:

... term quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

The sintering operation of the powder mixture is carried out at temperature which is higher than 600° C. but is not higher than the lowest melting point of any component in the material powder to be sintered. If the sintering temperature exceeds the ...

FOCUS - 35 OF 107 PATENTS

5,401,715

<=2> GET 1st DRAWING SHEET OF 1

Mar. 28, 1995

Semiconductor substrate having a superconducting thin film

INVENTOR: Itozaki, Hideo, Hyogo, Japan  
Harada, Keizo, Hyogo, Japan  
Fujimori, Naoji, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

DETDISC:

... term quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

An atomic ratio of the lanthanide element "Ln":Ba:Cu is preferably 1:2:3 as is defined by the formula but the atomic ratio is not restricted strictly to this ratio. In fact, the other compound oxides having ...

FOCUS - 36 OF 107 PATENTS

5,389,603

<=2> GET 1st DRAWING SHEET OF 5

Feb. 14, 1995

Oxide superconductors, and devices and systems comprising  
such a superconductor

INVENTOR: Batlogg, Bertram J., New Providence, New Jersey  
Cava, Robert J., Bridgewater, New Jersey

DETDISC:

... microscopy indicate a basically orthorhombic crystal structure, but there are also indications that, at least for some of the inventive compounds, the structure may be weakly monoclinic. Both of these possibilities are intended to be included in the term "perovskite-like" or analogous terms. Diffraction studies have also revealed the presence of a variety of long period long range ordered superlattices (typically in the ab plane).

FIG. 2 shows the field (225 Oe)-cooled ...

We claim:

[\*1] 1. An article comprising a superconductive element comprising at least one superconductive material having a perovskite-like crystal structure and nominal formula  $(\text{Pb}_{2A} \text{Cu}')\text{BCu}_{208} + \delta$  with (A selected from the group consisting of Sr, Ba, Sr and Ba, Sr and Ca, and Sr, Ba and Ca; Cu' is selected from the group consisting of ...

... [\*1] parallel to the ab- plane; and wherein the composition is selected such that the superconductive material has a transition temperature of at least about 30K.

[\*2] 2. An article comprising a superconductive element comprising at least one superconductive material having a perovskite-like crystal structure and nominal formula  $(\text{X}_{2A} \text{Cu}')\text{BCu}_{208} + \delta$ , where X is selected from the group consisting of Pb, Pb and Bi, Pb and Tl, and Pb, Bi and Tl, with X being at least 50 atomic % of ...

FOCUS - 37 OF 107 PATENTS

5,362,710

<=2> GET 1st DRAWING SHEET OF 2

Nov. 8, 1994

Process for preparing high Tc superconducting material

INVENTOR: Fujita, Nobuhiko, Hyogo, Japan  
Kobayashi, Tadakazu, Hyogo, Japan  
Itozaki, Hideo, Hyogo, Japan  
Tanaka, Saburo, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

SUM:

... quasi-perovskite type oxide means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

The present invention also provides a process for producing the abovementioned superconducting material, characterized by sintering a mixture of the following powders:

an oxide, carbonate, nitrate or sulfate of one element "A" selected from ...

FOCUS - 38 OF 107 PATENTS

5,356,674

<=2> GET 1st DRAWING SHEET OF 2

Oct. 18, 1994

Process for applying ceramic coatings using a plasma jet carrying a free form non-metallic element

INVENTOR: Henne, Rudolf, Boeblingen, Federal Republic of Germany  
Weber, Winfried, Leinfelden-Echterdingen, Federal Republic of Germany  
Schiller, Guenter, Gerlingen, Federal Republic of Germany  
Schnurnberger, Werner, Stuttgart, Federal Republic of Germany  
Kabs, Michael, Hanau, Federal Republic of Germany

SUM:

... materials are oxidized materials, for example, spinels and perovskites on a nickel or cobalt or nickel-cobalt basis. It is, however, also conceivable to apply all possible kinds of spinels and perovskites in accordance with the inventive process. This also applies to spinel-like and perovskite-like compounds and to non oxidized compounds, for example, nitrides, halides, carbides, etc., with nitrogen or halogens or also non-metallic compounds,

methane or acetylene the ... being carried along as non-metallic element by the ...  
FOCUS - 39 OF 107 PATENTS

5,354,733

<=2> GET 1st DRAWING SHEET OF 21

Oct. 11, 1994

Copper oxide superconductor containing carbonate radicals

INVENTOR: Kinoshita, Kyoichi, Hoya, Japan  
Yamada, Tomoaki, Higashimurayama, Japan

SUM:

... 2. Description of the Prior Art

Several types of copper oxide superconductors have been discovered since high-T c superconductivity was detected in the La-Ba-Cu-O system. Superconductivity would arise from the layered perovskite-like structure having CuO6 octahedra, or CuO5 pyramids, or CuO2 square planes as a building unit. The layered perovskite-like structure and a sufficient carrier concentration of the material are essential factors for making the material superconducting as indicated by Osamura & Zhang (Japan.J.Appl.Phys.26, L2094-L2096, 1987). ...

FOCUS - 40 OF 107 PATENTS

5,340,796

<=2> GET 1st DRAWING SHEET OF 5

Aug. 23, 1994

Oxide superconductor comprising Cu, Bi, Ca and Sr

INVENTOR: Cava, Robert J., Bridgewater, New Jersey  
Sunshine, Steven A., Berkeley Heights, New Jersey

ABST:

Novel superconductive oxides are disclosed. The oxides all have layered perovskite-like crystal structure and manifest superconductivity above about 77K. An exemplary material has composition Bi<sub>2.2</sub>Sr<sub>2</sub>Ca<sub>0.8</sub>Cu<sub>20</sub>8. Other materials are described by the nominal formula X<sub>2</sub> + x M n - x Cu n - ...

SUM:

... high temperature superconductors has been reported since publication of the above seminal papers. Most of the work deals with YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> (the so-called 1-2-3 compound) and related compounds.

In all of these compounds the superconducting phase is perovskite-like, typically having orthorhombic crystal structure, and the compounds that exhibit high (i.e., T c > 77K) temperature superconductivity generally contain one or more rare earth elements.

The discovery of high T c superconductivity in some ...

... likely to be stable high T c superconductors, with T c s likely to be above 100K.

The novel phases all have a crystal structure that is closely related to that of the above described 80K compound and thus are perovskite-like. They differ from each other essentially only in the number of crystal planes between the two Bi-O double planes that bound the unit cell in the c-direction, or by the size of the supercell. The composition of the ...

DETDISC:

... in added layers of M and Cu between the Bi-O double layers and are expected to result in one or more phases of stable high T c superconductive

material.

All of the inventive phases have layered perovskite-like crystal structure, and the existence of relatively weak bonding between at least some layers may be the cause of the observed relatively high ductility of the inventive materials. It will be appreciated that by "perovskite-like" we mean not only the prototypical, truly cubic structure, but very significantly distortions therefrom.

Material specification in accordance with the invention depends upon the nature of the intended use. For power transmission, or any other currentcarrying

...

Pat. No. 5340796, \*

PAGE

FOCUS

What is claimed is:

[\*1] 1. An article comprising material perovskite-like structure and of nominal composition  $X_2 + x M_4 - x Cu_{30}I_{10} + 0.5 \pm \delta$ , where  $[x = p/q < 0.4]$ , and p and q are positive integers]  $0 \leq x < 0.4$ , X is Bi and Pb, ...

FOCUS - 41 OF 107 PATENTS

5,338,721

<=2> GET 1st DRAWING SHEET OF 5

Aug. 16, 1994

Process for manufacturing a superconducting composite

INVENTOR: Yamamoto, Susumu, Hyogo, Japan  
Murai, Teruyuki, Hyogo, Japan  
Kawabe, Nozomu, Hyogo, Japan  
Awazu, Tomoyuki, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

DETDESC:

... quasi-perovskite type structure" means any oxide that can be considered to have such a crystal structure that is similar to perovskite-type oxides and may include an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

In practice, the element alpha is preferably selected from Ba, Sr and/or Ca and the element beta is preferably selected from Y, La and/or lanthanid such as Sc, Ce, Gd, Ho, Er, Tm, Yb, Lu and the ...

FOCUS - 42 OF 107 PATENTS

5,332,722

<=2> GET 1st DRAWING SHEET OF 3

Jul. 26, 1994

Nonvolatile memory element composed of combined  
superconductor ring and MOSFET

INVENTOR: Fujihira, Mitsuka, Yokohama, Japan

DETDESC:

... term quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

Another superconducting compound oxide which can be used by the present invention is represented by the general formula:

C24

(M,Sr)<sub>2</sub>CuO 4- delta

in which M stands for Y or La and ...

FOCUS - 43 OF 107 PATENTS

5,328,892

Jul. 12, 1994

Oxide superconductor composition and a process for the  
production thereof

INVENTOR: Manako, Takashi, Tokyo, Japan  
Shimakawa, Yuichi, Tokyo, Japan  
Kubo, Yoshimi, Tokyo, Japan

SUM:

... following formulae:

TlSr 3 - x Y x Cu<sub>2</sub>O<sub>7</sub>(IA)

wherein  $0.1 \leq x \leq 1$ , and

TlSr 4 - x Y x Cu<sub>3</sub>O<sub>9</sub>(IB)

wherein  $0.1 \leq x \leq 2$ . Unit cells of the layered perovskite-like crystal structures of these compositions of the formulae (IA) and (IB) may be shown respectively as follows:

TlO/SrO/CuO<sub>2</sub>/Sr or Y/CuO<sub>2</sub>/SrO(IX)

TlO/SrO/CuO<sub>2</sub>/Sr or Y/ ...

FOCUS - 44 OF 107 PATENTS

5,296,458

<=2> GET 1st DRAWING SHEET OF 4

Mar. 22, 1994

Epitaxy of high T<sub>c</sub> superconducting films on (001) silicon  
surface

INVENTOR: Himpel, Franz J., Mt. Kisco, New York

SUM:

... first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure. Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O system have been found to exhibit a superconducting transition temperature in excess of 77K.

R. B. ...

FOCUS - 45 OF 107 PATENTS

5,286,712

<=2> GET 1st DRAWING SHEET OF 2

Feb. 15, 1994

High TC superconducting film

INVENTOR: Fujita, Nobuhiko, Hyogo, Japan  
Kobayashi, Tadakazu, Hyogo, Japan

C25

Itozaki, Hideo, Hyogo, Japan  
Tanaka, Saburo, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

SUM:

... quasi-perovskite type oxide means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

The present invention also provides a process for producing the abovementioned superconducting material, characterized by sintering a mixture of the following powders:

an oxide, carbonate, nitrate or sulfate of one element "A" selected from ...  
FOCUS - 46 OF 107 PATENTS

5,283,465

<=2> GET 1st DRAWING SHEET OF 5

Feb. 1, 1994

Superconducting lead on integrated circuit

INVENTOR: Yamazaki, Shunpei, Tokyo, Japan

DETDESC:

... subjected to supplemental annealing at 500o-600o C. for 1-2 hours as illustrated in FIG. 1(B). The supplemental annealing allows the superconducting ceramic material to form a modulated perovskite-like structure and, as a result, a high critical temperature is realized. On the substrate, there are provided superconducting leads 10 and 10' for interconnection among devices and contacts formed in or on the semiconductor substrate and a ...

FOCUS - 47 OF 107 PATENTS

5,278,140

<=2> GET 1st DRAWING SHEET OF 5

Jan. 11, 1994

Method for forming grain boundary junction devices using  
high T c superconductors

INVENTOR: Chaudhari, Praveen, Briarcliff Manor, New York  
Chi, Cheng-Chung J., Yorktown Heights, New York  
Dimos, Duane B., Montclair, New Jersey  
Mannhart, Jochen D., Metzingen, New York, Federal Republic of Germany  
Tsuei, Chang C., Chappaqua, New York

SUM:

... first showed superconducting behavior in mixed copper-oxides, typically including rare earth and/or rare earth-like elements and alkaline earth elements, for example La, Ba, Sr, . . . , and having a perovskite-like structure. Materials including the so called "1-2-3" phase in the Y-Ba-Cu-O system have been found to exhibit a superconducting transition temperature in excess of 77K. R. B. ...

FOCUS - 48 OF 107 PATENTS

5,252,547

<=2> GET 1st DRAWING SHEET OF 1

Oct. 12, 1993



Method of forming an inorganic protective layer on an oxide  
superconducting film

INVENTOR: Itozaki, Hideo, Hyogo, Japan  
Tanaka, Saburo, Hyogo, Japan  
Fujita, Nobuhiko, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

SUM:

... term of quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to Perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

The superconducting thin film may be also another type of superconductor consisting mainly of a compound oxide represented by the formula:

THETA  $4(\text{PHI } 1 - q, \text{Ca } q) m \text{ Cu} \dots$   
FOCUS - 49 OF 107 PATENTS

5,249,525

<=2> GET 1st DRAWING SHEET OF 11

Oct. 5, 1993

Spark-discharge lithography plates containing image-support  
pigments

INVENTOR: Lewis, Thomas E., E. Hampstead, New Hampshire  
Nowak, Michael T., Gardner, Massachusetts

DETDESC:

... A perspective view of the first layer, labeled "Layer 0", appears in FIG. 6E. As shown in these figures, the spinel structure contains a number of octahedral sites for metal ions. Like perovskite structures spinels may also be defective, an example being gamma-Fe<sub>2</sub>O<sub>3</sub>. A spinel structure may also be intergrown with other structures.

In spinel compounds useful as image-support pigments, the ...  
FOCUS - 50 OF 107 PATENTS

5,244,874

Sep. 14, 1993

Process for producing an elongated superconductor

INVENTOR: Yamamoto, Susumu, Hyogo, Japan  
Kawabe, Nozomu, Hyogo, Japan  
Awazu, Tomoyuki, Hyogo, Japan

DETDESC:

... term quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

Another superconducting compound oxide which can be prepared by the present invention is represented by the general formula:

(M, Sr)<sub>2</sub>CuO<sub>4 - delta</sub>

in which M stands for Y or La and ...

FOCUS - 51 OF 107 PATENTS

5,241,191

<=2> GET 1st DRAWING SHEET OF 1

Aug. 31, 1993

Cubic perovskite crystal structure, a process of preparing the crystal structure, and articles constructed from the crystal structure

INVENTOR: Agostinelli, John A., Rochester, New York  
Chen, Samuel, Penfield, New York

DETDESC:

... 1, PA-2, PA-3, PA-4 and PA-5, cited above and here incorporated by reference, can be employed. Highly compatible substrates are materials that themselves exhibit a perovskite or perovskite-like crystal structure. Strontium titanate is an example of a perovskite crystal structure which is specifically preferred for use as a substrate. Lanthanum aluminate ( $\text{LaAlO}_3$ ), lanthanum gallium oxide ( $\text{LaGaO}_3$ ) and potassium tantalate are ...

FOCUS - 52 OF 107 PATENTS

5,236,894

Aug. 17, 1993

Process for producing a superconducting thin film at relatively low temperature

INVENTOR: Tanaka, Saburo, Itami, Japan  
Itozaki, Hideo, Itami, Japan  
Higaki, Kenjiro, Itami, Japan  
Yazu, Shuji, Itami, Japan  
Jodai, Tetsuji, Itami, Japan

SUM:

... crystal structure. The term quasi-perovskite type means a structure which can be considered to be similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

Still another example of the above-mentioned compound oxide is compound oxides represented by the general formula:

$\text{THETA } 4(\text{PHI } 1 - q, \text{Ca } q) \text{ m Cu n O p} + \dots$

FOCUS - 53 OF 107 PATENTS

5,221,660

<=2> GET 1st DRAWING SHEET OF 1

Jun. 22, 1993

Semiconductor substrate having a superconducting thin film

INVENTOR: Itozaki, Hideo, Hyogo, Japan  
Harada, Keizo, Hyogo, Japan  
Fujimori, Naoji, Hyogo, Japan  
Yazu, Shuji, Hyogo, Japan  
Jodai, Tetsuji, Hyogo, Japan

DETDESC:

... term quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

An atomic ratio of lanthanide element "Ln":Ba:Cu preferably 1:2:3 as is defined by the formula but the atomic ratio is not restricted strictly to this ratio. In fact, the other compound oxides having ...

FOCUS - 54 OF 107 PATENTS

5,212,148

<=2> GET 1st DRAWING SHEET OF 1

May 18, 1993

Method for manufacturing oxide superconducting films by  
laser evaporation

INVENTOR: Roas, Bernhard, Erlangen, Federal Republic of Germany  
Endres, Gerhard, Forchheim, Federal Republic of Germany  
Schultz, Ludwig, Bubenreuth, Federal Republic of Germany

SUM:

... yet exactly established. This initial product is then converted, by applying a heat and oxygen treatment, into the material with the desired superconducting phase.

The superconductive metal-oxide phases, to be obtained in this manner, can have perovskite-like crystal structures and, in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , whereby  $0 < x < 0.5$ , have an orthorhombic structure (compare, for example, "Europhysics Letters", Vol. 3, No. 12, Jun. 15, 1987, pages ...

FOCUS - 55 OF 107 PATENTS

5,183,799

<=2> GET 1st DRAWING SHEET OF 16

Feb. 2, 1993

Superconducting materials including La-Sr-Nb-O, Y-Ba-Nb-O,  
La-Sr-Nb-Cu-O, and Y-Ba-Nb-Cu-O

INVENTOR: Ogushi, Tetsuya, Kagoshima, Japan  
Hakuraku, Yoshinori, Kagoshima, Japan  
Ogata, Hisanao, Ibraki, Japan

ABST:

... V, Nb, Ta, T, Zr or Hf;  $0 < x < 1$ ;  $0 < z < 1$ ;  $i = 1, 3/2$  or  $2$ ;  $0 < y \leq 4$ ; G is F, Cl or N; delta is oxygen defect, and having a perovskite-like crystal structure, show superconductivity at a temperature higher than the liquid nitrogen temperature.

SUM:

BACKGROUND OF THE INVENTION

This invention relates to a superconducting material having a perovskite-like crystal structure and a superconducting part using the same, particularly to a superconducting material suitable for having a high superconducting transition temperature ( $T_c$ ), and a process for producing the same.

Heretofore, ...

DETDISC:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The superconducting materials of this invention have a perovskite-like crystal structure and represented by the formulae:

$(L x A 1 - x) i MO (1)$

$(L x A 1 - x) i M 1 - z Cu z \dots$

... by laminating this superconducting material with other films of electrical insulating material. It is preferable to laminate a plurality of film-like layers alternately, respectively. Further, it is preferable to use as an insulating material a perovskite-like ceramic of the same series.

Further, in the above-mentioned formulae (1) and (2), a total of valence number (p) of L, A and M, or L, A, M and Cu, and the valence number y of ...

... OMITTED p SYMBOL OMITTED = SYMBOL OMITTED y SYMBOL OMITTED +/- 0.5

Pat. No. 5183799, \*

FOCUS

Further, it is preferable to include M of the valence of two.

More in detail, the material represented by the formula (1) has a perovskite-like crystal structure and has as the L element at least one element selected from the group consisting of scandium (Sc), yttrium (Y), and lanthanide elements of atomic numbers 57 to 71 (La to Lu) belonging to the group ...

... Ta) belonging to the group Vb of the periodic table and titanium (Ti), zirconium (Zr) and hafnium (Hf) belonging to the group IVb of the periodic table, these element being able to include Cu.

The oxide superconducting material having the perovskite-like crystal structure of this invention has as a fundamental constitution an octahedron having the M element which is an atom belonging to the group Vb or IVb as its center and 6 oxygen atoms. Since this material has defect of oxygen, that is, one or ...

... a mutual action of strong attraction necessary for forming a hole pair or electron pair showing a superconducting phenomenon at a temperature of 150K or higher.

The oxide superconducting material of this invention has the perovskite-like crystal structure as shown in FIGS. 1 and 2. These drawings show unit lattices of the materials represented by the formulae:

$(L x A 1 - x) i MO y (1)$

and ( ...

... formula (4) with at least one element selected from those of the group IVb and Vb, the total amount of the elements of the group IVb and Vb can exceed the amount of Cu.

It is also possible to produce an oxide superconducting powder having a perovskite-like crystal structure containing M element mainly by mixing a powder of oxide material represented by  $(L x A 1 - x) i CuO y$ , wherein x is  $0 < x < 1$ ; ...

... Cu:M = 1:1, carrying out substitution reaction between Cu and M element in vacuum, and finally pulverizing the final reaction product.

It is further possible to produce an oxide superconducting powder having a perovskite-like crystal structure and containing M element mainly by depositing in vacuum a film of pure metal of M element selected from the elements of groups IVb and Vb on outer surface of oxide ceramic ...

... 1, 3/2 or 2; y is  $0 < y \leq 4$ , containing the M element mainly (M being

Attachment D

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LEVEL 1 - 1 OF 2 PATENTS

5,134,042

<=2> GET 1st DRAWING SHEET OF 6

Jul. 28, 1992

Solid compositions for fuel cells, sensors and catalysts

INVENTOR: Madou, Marc J., Palo Alto, California  
Otagawa, Takaaki, Fremont, California  
Sher, Arden, Foster City, California

... [\*12] selected from lanthanum, cerium, neodymium, praseodymium, or scandium, B is independently selected from strontium, calcium, barium or magnesium, Q is independently selected from nickel, cobalt, iron or manganese, and y is between about 0.0001 and 1, wherein the perovskite or perovskite-type structure has an average size and distribution of between about 50 and 200 Angstroms in diameter; and the composite layer of between about 25 and 1000 microns in thickness;

DI

said composite having multiple interfaces between:

PAGE

LEVEL 1 - 2 OF 2 PATENTS

4,948,680

<=2> GET 1st DRAWING SHEET OF 26

Aug. 14, 1990

Solid compositions for fuel cell electrolytes

INVENTOR: Madou, Marc J., Palo Alto, California  
Otagawa, Takaaki, Fremont, California  
Sher, Arden, Foster City, California

... [\*25] 1.5 and d is between 0.001 and less than or equal to 3,

wherein either the first electrode material (C) or second electrode material (A') comprises

$A_1 - x B_x Q_0_3$

having a perovskite or perovskite-type structure as an electrode catalyst in combination with

$A_1 - x B_x Z$

as a polycrystalline solid electrolyte wherein

A is independently selected from lanthanum, cerium, neodymium, praseodymium or scandium,

\* 2 PAGES

36 LINES

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11/24/97

\*

D2

Attachment E



# Perovskites and High $T_c$ Superconductors

by

Francis S. Galasso

*United Technologies Research Laboratories  
East Hartford, Connecticut  
USA*

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FL

these compounds as described. In addition, a few oxides with the

perovskite bubble research, high dielectric constant memory work and research conducted for the use of interest in devices have been investigated

There is more interest in perovskite than that the greatest part of the discovery of the perovskite is devoted to this

## Chapter II

# Structure of Perovskite-type Compounds

Most of the compounds with the general formula  $ABO_3$  have the perovskite structure. The atomic arrangement in this structure was first found for the mineral perovskite,  $CaTiO_3$ . It was thought that the unit cell of  $CaTiO_3$  could be represented by calcium ions at the corners of a cube with titanium ions at the body center and oxygen ions at the center of the faces (Fig. 2.1). This simple cubic structure has retained the name perovskite, even though  $CaTiO_3$  was later determined to be orthorhombic by Megaw.<sup>(1)</sup> Through the years it has been found that very few perovskite-type oxides have the simple cubic structure at room temperature, but many assume this ideal structure at higher temperatures.

In the perovskite structure, the A cation is coordinated with twelve oxygen ions and the B cation with six. Thus, the A cation is normally found to be somewhat larger than the B cation. In order to have contact between the A, B, and O ions,  $R_A + R_O$  should equal  $\frac{\sqrt{2}}{2}(R_B + R_O)$ , where  $R_A$ ,  $R_B$  and  $R_O$  are the ionic radii. Goldschmidt<sup>(2)</sup> has shown that the cubic perovskite structure is stable only if a tolerance factor,  $t$  defined by  $R_A + R_O = t\frac{\sqrt{2}}{2}(R_B + R_O)$ , has an approximate range of  $0.8 < t < 0.9$ , and a somewhat larger range for distorted perovskite structures. It should be noted that conflicting reports in the literature make it difficult to assign the correct unit cell dimensions for these distorted perovskite structures.

The ternary perovskite-type oxides described in this chapter will be divided into  $A^{1+}B^{5+}O_3$ ,  $A^{2+}B^{4+}O_3$ ,  $A^{3+}B^{3+}O_3$  types and oxygen- and cation-deficient phases. The oxygen- and cation-deficient phases will be regarded as those which contain considerable vacancies and not those phases which are only slightly non-stoichiometric. Many of these contain B ions of one element in two valence states and should

Attachment F

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# COPPER OXIDE SUPERCONDUCTORS

---

**Charles P. Poole, Jr.**  
**Timir Datta**  
**Horacio A. Farach**

*with help from*

**M. M. Rigney**  
**C. R. Sanders**

*Department of Physics and Astronomy  
University of South Carolina  
Columbia, South Carolina*



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F1

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F2

tetragonal phase, and the metal-to-insulator transition occurs at the tetragonal-to-orthorhombic phase boundary  $x \approx 0.35$  (Matt7, Sleil).

#### D. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller referred to their samples as "metallic, oxygen deficient . . . perovskite like mixed valent copper compounds." Subsequent work has confirmed that the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects.

##### 1. Atom Sizes

In the oxide superconductors Cu replaces the  $Ti^{4+}$  ions ( $0.68 \text{ \AA}$ ) of perovskite, and in most cases retains the  $CuO_2$  layering with two oxygens per copper in the layer. Other cationic replacements tend to be Bi, Ca, La, Sr, Tl, and Y for the larger Ba, forming "layers" containing only one oxygen or none per cation. We see from the following list of ionic radii

|           |                    |        |
|-----------|--------------------|--------|
| $Cu^{2+}$ | $0.72 \text{ \AA}$ |        |
| $Bi^{5+}$ | $0.74 \text{ \AA}$ |        |
| $Y^{3+}$  | $0.94 \text{ \AA}$ |        |
| $Tl^{3+}$ | $0.95 \text{ \AA}$ |        |
| $Bi^{3+}$ | $0.96 \text{ \AA}$ |        |
| $Ca^{2+}$ | $0.99 \text{ \AA}$ | (VI-4) |
| $Sr^{2+}$ | $1.12 \text{ \AA}$ |        |
| $La^{3+}$ | $1.14 \text{ \AA}$ |        |
| $Ba^{2+}$ | $1.34 \text{ \AA}$ |        |
| $O^{2-}$  | $1.32 \text{ \AA}$ |        |

that there are four size groups, with all other cations significantly smaller than the Ba of perovskite. The common feature of  $CuO_2$  layers that are planar or close to planar establishes a fairly uniform lattice size in the  $a, b$  plane. The parameters of the compounds  $LaSrCuO$  ( $a = b = 3.77 \text{ \AA}$ ),  $YBaCuO$  ( $a = 3.83 \text{ \AA}$ ,  $b = 3.89 \text{ \AA}$ ),  $BiSrCaCuO$  ( $a = b = 3.82 \text{ \AA}$ ), and  $TlBaCaCuO$  ( $a = b = 3.86 \text{ \AA}$ ) are all between the ideal fcc oxygen lattice value of  $3.73 \text{ \AA}$  and the perovskite one of  $4.01 \text{ \AA}$ .

Table VI-2 gives the ionic radii of the positively charged ions of various elements of the periodic table. These radii are useful for estimating changes in lattice constant when ionic substitutions are made in existing structures. They also provide some insight into which types of substitutions will be most favorable.

on occurs at the tetragonal-Sleil).

## STRUCTURES

ctors Bednorz and Müller  
icient . . . perovskite like  
has confirmed that the new  
cs. In this section we will

ns (0.68 Å) of perovskite,  
oxygens per copper in the  
La, Sr, Tl, and Y for the  
en or none per cation. We

(VI-4)

significantly smaller than  
s that are planar or close  
a,b plane. The paramete-  
aCuO ( $a = 3.83$  Å,  $b =$   
CuO ( $a = b = 3.86$  Å)  
73 Å and the perovskite

arged ions of various ele-  
timating changes in lat-  
ng structures. They also  
will be most favorable.

TABLE VI-2. Ionic Radii in Angstroms of Selected Elements for Various Positive Charge States<sup>a</sup>

| Z   | Element | +1   | +2   | +3   | +4   | +5   | +6   |
|---|---------|------|------|------|------|------|------|
| <i>Alkali</i>                                   |         |      |      |      |      |      |      |
| 3   | Li      | 0.68 |      |      |      |      |      |
| 11  | Na      | 0.97 |      |      |      |      |      |
| 19  | K       | 1.33 |      |      |      |      |      |
| 37  | Rb      | 1.47 |      |      |      |      |      |
| 55  | Cs      | 1.67 |      |      |      |      |      |
| <i>Alkaline earths</i>                          |         |      |      |      |      |      |      |
| 4   | Be      | 0.44 | 0.35 |      |      |      |      |
| 12  | Mg      | 0.82 | 0.66 |      |      |      |      |
| 20  | Ca      | 1.18 | 0.99 |      |      |      |      |
| 38  | Sr      |      | 1.12 |      |      |      |      |
| 56  | Ba      | 1.53 | 1.34 |      |      |      |      |
| <i>Group III</i>                                |         |      |      |      |      |      |      |
| 5   | B       | 0.35 |      | 0.23 |      |      |      |
| 13  | Al      |      |      | 0.51 |      |      |      |
| 31  | Ga      | 0.81 |      | 0.62 |      |      |      |
| 49  | In      |      |      | 0.81 |      |      |      |
| 81  | Tl      | 1.47 |      | 0.95 |      |      |      |
| <i>Group IV</i>                                 |         |      |      |      |      |      |      |
| 6   | C       |      |      |      | 0.16 |      |      |
| 14  | Si      | 0.65 |      |      | 0.42 |      |      |
| 32  | Ge      |      | 0.73 |      | 0.53 |      |      |
| 50  | Sn      |      | 0.93 |      | 0.71 |      |      |
| 82  | Pb      |      | 1.20 |      | 0.84 |      |      |
| <i>Group V</i>                                  |         |      |      |      |      |      |      |
| 15  | P       |      |      | 0.44 |      | 0.35 |      |
| 33  | As      |      |      | 0.58 |      | 0.46 |      |
| 51  | Sb      | 0.89 |      | 0.76 |      | 0.62 |      |
| 83  | Bi      | 0.98 |      | 0.96 |      | 0.74 |      |
| <i>Chalcogenides</i>                            |         |      |      |      |      |      |      |
| 16  | S       |      |      |      | 0.37 |      | 0.30 |
| 34  | Se      | 0.66 |      |      | 0.50 |      | 0.42 |
| 52  | Te      | 0.82 |      |      | 0.70 |      | 0.56 |
| <i>First transition series (3d<sup>n</sup>)</i> |         |      |      |      |      |      |      |
| 21  | Sc      |      |      | 0.81 |      |      |      |
| 22  | Ti      | 0.96 | 0.94 | 0.76 | 0.68 |      |      |
| 23  | V       |      | 0.88 | 0.74 | 0.63 | 0.59 |      |
| 24  | Cr      | 0.81 | 0.89 | 0.63 |      |      | 0.52 |
| 25  | Mn      |      | 0.80 | 0.66 | 0.60 |      |      |



TABLE VI-2. (continued)

| Z  | Element | +1   | +2   | +3   | +4   | +5   | +6   |
|--|---------|------|------|------|------|------|------|
| 26   | Fe      |      | 0.74 | 0.64 |      |      |      |
| 27   | Co      |      | 0.72 | 0.63 |      |      |      |
| 28   | Ni      |      | 0.69 |      |      |      |      |
| 29   | Cu      | 0.96 | 0.72 |      |      |      |      |
| 30   | Zn      | 0.88 | 0.74 |      |      |      |      |
| <i>Second transition series (4d<sup>n</sup>)</i> |         |      |      |      |      |      |      |
| 39   | Y       |      |      | 0.94 |      |      |      |
| 40   | Zr      | 1.09 |      |      | 0.79 |      |      |
| 41   | Nb      | 1.00 |      |      | 0.74 | 0.69 |      |
| 42   | Mo      | 0.93 |      |      | 0.70 |      | 0.62 |
| 43   | Tc      |      |      |      |      |      |      |
| 44   | Ru      |      |      |      | 0.67 |      |      |
| 45   | Rh      |      |      | 0.68 |      |      |      |
| 46   | Pd      |      | 0.80 |      | 0.65 |      |      |
| 47   | Ag      | 1.26 | 0.89 |      |      |      |      |
| 48   | Cd      | 1.14 | 0.97 |      |      |      |      |
| <i>Third transition series (5d<sup>n</sup>)</i>  |         |      |      |      |      |      |      |
| 72   | Hf      |      |      |      | 0.78 |      |      |
| 73   | Ta      |      |      |      |      | 0.68 |      |
| 74   | W       |      |      |      | 0.70 |      | 0.62 |
| 75   | Re      |      |      |      | 0.72 |      |      |
| 76   | Os      |      |      |      | 0.88 |      | 0.69 |
| 77   | Ir      |      |      |      | 0.68 |      |      |
| 78   | Pt      |      | 0.80 |      | 0.65 |      |      |
| 79   | Au      | 1.37 |      | 0.85 |      |      |      |
| 80   | Hg      | 1.27 | 1.10 |      |      |      |      |
| <i>Rare earths (4f<sup>n</sup>)</i>              |         |      |      |      |      |      |      |
| 57   | La      | 1.39 |      | 1.14 |      |      |      |
| 58   | Ce      | 1.27 |      | 1.07 | 0.94 |      |      |
| 59   | Pr      |      |      | 1.06 | 0.92 |      |      |
| 60   | Nd      |      |      | 1.04 |      |      |      |
| 61   | Pm      |      |      | 1.06 |      |      |      |
| 62   | Sm      |      |      | 1.00 |      |      |      |
| 63   | Eu      |      |      | 0.98 |      |      |      |
| 64   | Gd      |      |      | 0.62 |      |      |      |
| 65   | Tb      |      |      | 0.93 | 0.81 |      |      |
| 66   | Dy      |      |      | 0.92 |      |      |      |
| 67   | Ho      |      |      | 0.91 |      |      |      |
| 68   | Er      |      |      | 0.89 |      |      |      |
| 69   | Tm      |      |      | 0.87 |      |      |      |
| 70   | Yb      |      |      | 0.86 |      |      |      |
| 71   | Lu      |      |      | 0.85 |      |      |      |

\*Three anion radii are 1.32 for O<sup>2-</sup>, 1.33 for F<sup>-</sup>, and 1.84 for S<sup>2-</sup> (*Handbook of Chemistry and Physics*).

Attachment G

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# COPPER OXIDE SUPERCONDUCTORS

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# VI

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## CRYSTALLOGRAPHIC STRUCTURES

### A. INTRODUCTION

To properly understand the mechanisms that bring about the superconducting state in particular materials it is necessary to know the structures of the compounds that exhibit this phenomenon. Single-crystal structure studies have been carried out to determine the dimensions of the unit cell, the locations of the atoms in this cell, electronic charge distributions, and the possible presence of atomic irregularities. Neutron powder diffraction has also provided much of the detailed structure information found in this chapter (e.g., Antso, Beech, Cappo, Coxzz, Davi1, Dayzz, Greed, John4, Jorge, Jorg1, Paulz, Torar, Vakni, Yamag, Yanz2). More routine X-ray powder pattern measurements which can identify a known structure and provide the unit cell dimensions are useful for checking the quality of samples, as was explained in Section V-1.

The numerical values of quantities such as lattice parameters and bond lengths show some variation in the literature, and many of our quoted values will be typical ones. Much of the quantitative structural information is organized in the tables.

In the beginning of this chapter we will introduce the perovskite structure and indicate how it is related to the oxide superconductors. Then we will describe the 21 structure of LaSrCuO and the 123 structure of YBaCuO, we will show how each is generated from a perovskite prototype, and we will clarify its layering scheme. The chapter will end with descriptions of the structures of the newer high-transition-temperature bismuth and thallium compounds.

## B. PEROVSKITES

Much has been written about the oxide superconductor compounds being perovskite types, so we will begin with a description of the perovskite structure. This will permit us to develop some of the notation to be used in describing the structures of the superconductors themselves.

### 1. Cubic Form

Above 200°C barium titanate crystallizes in the perovskite structure, which is cubic, so the three lattice parameters are all equal (i.e.,  $a = b = c$ ). The unit cell contains one formula unit  $\text{BaTiO}_3$  and the atoms are located in the following special positions (Wyck2, p. 390):

|    |      |   |        |
|----|------|---|--------|
| Ba | (1a) | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$             | (VI-1) |
| Ti | (1b) | 0,0,0   |        |
| O  | (3c) | $0,0,\frac{1}{2}; 0,\frac{1}{2},0; \frac{1}{2},0,0$ |        |

where we have employed the crystallographic notation (1a) for an a-type lattice site which contains one atom, (3c) for a c-type lattice site which contains three atoms, and so on. Each atomic position is given by three coordinates, such as  $0,0,\frac{1}{2}$  for the oxygen located at  $x = 0, y = 0, z = 0.5a$ . This arrangement corresponds to placing a titanium atom on each apex, a barium atom in the body center, and an oxygen atom on the center of each edge of the cube, as illustrated on Fig. VI-1. We see from the figure that the barium atoms are 12-fold coordinated and the titaniums have sixfold (octahedral) coordination. The lattice constant or length of the unit cell is  $a = 4.0118 \text{ \AA}$  at 201°C. The crystallographic space group is  $Pm\bar{3}m, O_h^h$ .

An alternate way to represent this structure, which is commonly used in solid-state texts and in crystallography monographs (e.g., Wyck2), is to locate the

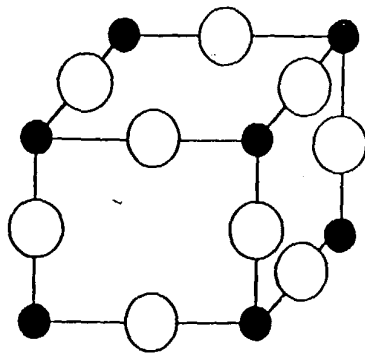


Fig. VI-1. Perovskite cubic unit cell showing titanium on the apices and oxygen in the edge-centered positions. Barium, which is in the body center, is not shown.

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origin at the barium site; this places titanium in the center and the oxygens on the centers of the cube faces. The representation (Eq. VI-1) given above is more convenient for comparison with the structures of the oxide superconductors.

The compound  $\text{LaBaCu}_2\text{O}_5$  was found to have a cubic perovskite subcell with the lattice parameter  $a = 3.917 \text{ \AA}$  (Sishe).

## 2. Tetragonal Form

At room temperature barium titanate is tetragonal with the unit cell dimensions  $a = 3.9947 \text{ \AA}$  and  $c = 4.0336 \text{ \AA}$ , which is close to cubic. For this lower symmetry the oxygens are assigned to two different sites, a single site along the side edges and a twofold one at the top and bottom. The atomic positions (Wyck2, p. 401)

$$\begin{array}{ll} \text{Ba} & \frac{1}{2}, \frac{1}{2}, 0.488 \\ \text{Ti} & 0, 0, 0 \\ \text{O}(1) & 0, 0, 0.511 \\ \text{O}(2) & 0, \frac{1}{2}, -0.026; \frac{1}{2}, 0, -0.026 \end{array} \quad (\text{VI-2})$$

are shown in Fig. VI-2. The distortions from the ideal structure of Fig. VI-1 are exaggerated on this sketch. We will see later that a similar distortion occurs in the  $\text{YBaCuO}$  structure. The cubic and tetragonal atom arrangements (VI-1) and (VI-2) are compared in Table VI-1, and we see from this table that the deviation from cubic symmetry is actually quite small.

## 3. Orthorhombic Form

When barium titanate is cooled below  $5^\circ\text{C}$  it undergoes a transition with a further lowering of the symmetry to the orthorhombic space group  $\text{Amm}2$ ,  $\text{C}_{2v}$ , and

TABLE VI-1. Comparison of Atom Positions of  $\text{BaTiO}_3$  in Its Cubic, Tetragonal and Orthorhombic Forms\*

| Group          | Atom | Cubic and Tetragonal |               | Cubic         | Tetragonal | Orthorhombic  |
|----------------|------|----------------------|---------------|---------------|------------|---------------|
|                |      | x                    | y             | z             | z          | z             |
| $\text{TiO}_2$ | Ti   | 0                    | 0             | 1             | 1          | 1             |
|                | O    | 0                    | $\frac{1}{2}$ | 1             | 0.974      | 1             |
|                | O    | $\frac{1}{2}$        | 0             | 1             | 0.974      | 1             |
| BaO            | O    | 0                    | 0             | $\frac{1}{2}$ | 0.511      | $\frac{1}{2}$ |
|                | Ba   | $\frac{1}{2}$        | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.488      | $\frac{1}{2}$ |
| $\text{TiO}_2$ | Ti   | 0                    | 0             | 0             | 0          | 0             |
|                | O    | 0                    | $\frac{1}{2}$ | 0             | -0.026     | 0             |
|                | O    | $\frac{1}{2}$        | 0             | 0             | -0.026     | 0             |

\*The x and y coordinates are the same for both positions. The orthorhombic form z coordinates are also given (Wyck2, pp. 390, 401, 405).

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roup  $Amm2$ ,  $C_{2v}$ , and

Cubic, Tetragonal and

| al | Orthorhombic  |
|----|---------------|
|    | $z$           |
|    | 1             |
|    | 1             |
|    | 1             |
|    | $\frac{1}{2}$ |
|    | $\frac{1}{2}$ |
|    | 0             |
|    | 0             |
|    | 0             |

bic form  $z$  coordinates are

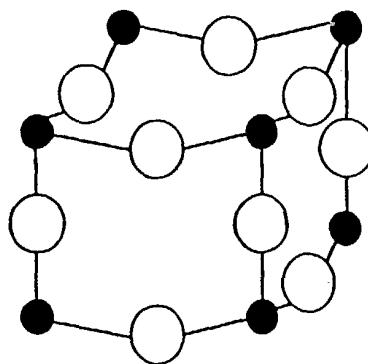


Fig. VI-2. Perovskite tetragonal unit cell showing the puckering of the Ti-O layers.

an enlargement of the unit cell to accommodate two formula units  $(BaTiO_3)_2$ . The enlarged cell is rotated by  $45^\circ$  relative to the higher-temperature ones, as shown on Fig. VI-3, and therefore its  $a$  and  $b$  lattice parameters are larger by the factor  $\sqrt{2}$ . The three lattice constants are  $a = 5.669 = 4.009\sqrt{2} \text{ \AA}$ ,  $b = 5.682 = 4.018\sqrt{2} \text{ \AA}$ , and  $c = 3.990 \text{ \AA}$ . There are no longer any special sites, and the atomic positions are (Wyck2, p. 405):

$$\begin{array}{ll}
 \text{Ba} & (2a) \quad 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2} \\
 \text{Ti} & (2b) \quad 0, u + \frac{1}{2}, 0; \frac{1}{2}, u, 0 \quad \text{with } u = 0.510 \\
 \text{O(1)} & (2a) \quad 0, u + \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, u, \frac{1}{2} \quad \text{with } u = 0.490 \\
 \text{O(2)} & (4e) \quad u, v + \frac{1}{2}, 0; -u, v + \frac{1}{2}, 0; u + \frac{1}{2}, v, 0; -u + \frac{1}{2}, v, 0 \\
 & \quad \text{with } u = 0.253, v = 0.237
 \end{array} \quad (VI-3)$$

where  $u = 0$  for Ba.

One should note that in Eq. (VI-3) Ba and O(1) are in the same (2a) type of site with different values of the parameter  $u$ . Figure VI-3 shows the coordinates of the atoms in the orthorhombic cell drawn using the approximation  $\approx \frac{1}{2}$  for 0.490 and 0.510 and  $\approx \frac{1}{4}$  for 0.253 and 0.237.

A comparison of Eqs. VI-1 to VI-3 indicates that the transformation from cubic to tetragonal involves only shifts in the  $z$  coordinates of atoms, while the orthorhombic phrase differs from the cubic one only through shifts in atom positions within  $x, y$  planes (see Table VI-1).

#### 4. Atom Arrangements

The ionic radii of  $Ba^{2+}$  (1.34  $\text{\AA}$ ) and  $O^{2-}$  (1.32  $\text{\AA}$ ) are almost the same, and together they form a face-centered cubic (fcc) close-packed lattice with the smaller  $Ti^{4+}$  ions (0.68  $\text{\AA}$ ) located in octahedral holes. The octahedral holes of a close-packed oxygen lattice have a radius of 0.545  $\text{\AA}$ , and if these holes were empty the lattice parameter would be  $a = 3.73$ , as shown on Fig. VI-4a. If each

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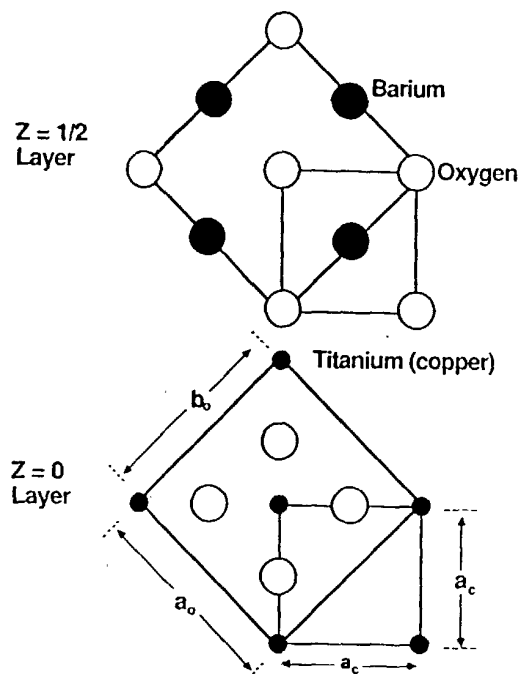


Fig. VI-3. Atom positions of perovskite when the monomolecular tetragonal unit cell is expanded to the bimolecular orthorhombic cell with new axes at  $45^\circ$  with respect to the old ones.

titanium were to move the surrounding oxygens apart to its ionic radius when occupying the hole, as shown on Fig. VI-4b, the lattice parameter  $a$  would be  $4.00 \text{ \AA}$ . The observed cubic ( $a = 4.012 \text{ \AA}$ ) and tetragonal ( $a = 3.995 \text{ \AA}$ ,  $c = 4.034 \text{ \AA}$ ) lattice parameters are close to these values, indicating a pushing apart of the oxygens. The tetragonal distortion illustrated on Fig. VI-2 and the orthorhombic distortion of Eq. (VI-3) constitute attempts to achieve this through an enlarged but distorted octahedral site. This same mechanism is operative in the oxide superconductors.

### C. BARIUM-LEAD-BISMUTH OXIDE

In 1983 Mattheiss and Hamann referred to the 1975 "discovery by Sleight et al. of high temperature superconductivity" of the compound  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  in the composition range  $0.05 \leq x \leq 0.3$  with  $T_c$  up to 13 K (Matt7, Sleig). Many consider this system, which disproportionates  $2 \text{ Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}$  in going from the metallic to the semiconducting state, as a predecessor to the  $\text{LaSrCuO}$  system.

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TABLE VI-3. Atom Positions of Regular and Alternate  $\text{La}_2\text{CuO}_4$  Structure, Both of Which Correspond to Space Group  $I4/mmm$ ,  $D_{4h}^{17a}$ 

| Complex               | Ideal $z$             | Regular Structure |      |               |               |               | Alternate Structure |      |               |               |               |
|-----------------------|-----------------------|-------------------|------|---------------|---------------|---------------|---------------------|------|---------------|---------------|---------------|
|                       |                       | Atom              | Site | $x$           | $y$           | $z$           | Atom                | Site | $x$           | $y$           | $z$           |
| $\text{CuO}_2$        | 1                     | O(1)              | 4c   | $\frac{1}{2}$ | 0             | 1             | O(1)                | 4c   | $\frac{1}{2}$ | 0             | 1             |
|                       |                       | O(1)              | 4c   | 0             | $\frac{1}{2}$ | 1             | O(1)                | 4c   | 0             | $\frac{1}{2}$ | 1             |
|                       |                       | Cu                | 2a   | 0             | 0             | 1             | Cu                  | 2a   | 0             | 0             | 1             |
| OLa                   | $\frac{5}{6} = 0.833$ | La                | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.862         | La                  | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.862         |
|                       |                       | O(2)              | 4e   | 0             | 0             | 0.818         |                     |      |               |               |               |
|                       |                       |                   |      |               |               |               | O(2)                | 4d   | 0             | $\frac{1}{2}$ | $\frac{3}{4}$ |
| LaO                   | $\frac{2}{3} = 0.667$ | O(2)              | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.682         | O(2)                | 4d   | $\frac{1}{2}$ | 0             | $\frac{3}{4}$ |
|                       |                       | La                | 4e   | 0             | 0             | 0.638         | La                  | 4e   | 0             | 0             | 0.638         |
|                       |                       | O(1)              | 4c   | 0             | $\frac{1}{2}$ | $\frac{1}{2}$ | O(1)                | 4c   | 0             | $\frac{1}{2}$ | $\frac{1}{2}$ |
| $\text{O}_2\text{Cu}$ | $\frac{1}{2}$         | O(1)              | 4c   | $\frac{1}{2}$ | 0             | $\frac{1}{2}$ | O(1)                | 4c   | $\frac{1}{2}$ | 0             | $\frac{1}{2}$ |
|                       |                       | Cu                | 2a   | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | Cu                  | 2a   | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |
|                       |                       | La                | 4e   | 0             | 0             | 0.362         | La                  | 4e   | 0             | 0             | 0.362         |
| LaO                   | $\frac{1}{3} = 0.333$ | O(2)              | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.318         |                     |      |               |               |               |
|                       |                       |                   |      |               |               |               | O(2)                | 4d   | $\frac{1}{2}$ | 0             | $\frac{1}{4}$ |
|                       |                       |                   |      |               |               |               | O(2)                | 4d   | 0             | $\frac{1}{2}$ | $\frac{1}{4}$ |
| OLa                   | $\frac{1}{6} = 0.167$ | O(2)              | 4e   | 0             | 0             | 0.182         |                     |      |               |               |               |
|                       |                       | La                | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.138         | La                  | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.138         |
|                       |                       | O(1)              | 4c   | $\frac{1}{2}$ | 0             | 0             | O(1)                | 4c   | $\frac{1}{2}$ | 0             | 0             |
| $\text{CuO}_2$        | 0                     | O(1)              | 4c   | 0             | $\frac{1}{2}$ | 0             | O(1)                | 4c   | 0             | $\frac{1}{2}$ | 0             |
|                       |                       | Cu                | 2a   | 0             | 0             | 0             | Cu                  | 2a   | 0             | 0             | 0             |
|                       |                       |                   |      |               |               |               |                     |      |               |               |               |

<sup>a</sup>Superconducting compounds crystallize in the regular structure (Oguch; see also Onoda). The ideal  $z$  values in column 2 are for the prototype perovskite.

constants for tetragonal  $\text{LaSrCuO}$  superconductors with various values of  $x$ ,  $y$ , and  $\delta$  in the formula  $(\text{La}_{1-x}\text{Sr}_x)_{2-y}\text{CuO}_{4-\delta}$ .

## 2. Alternate Tetragonal Form

In the previous section we discussed the tetragonal structure which is adopted by  $\text{LaSrCuO}$  superconductors. It has a variant (Hutir, Oguch) called the  $\text{Nd}_2\text{CuO}_4$  structure in which the oxygens O(2) are in special sites (4d) instead of the general (4e) sites in the same space group, corresponding to

$$\text{O}(2) \quad (4d) \quad 0, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, 0, \frac{1}{4}; \frac{1}{2}, 0, \frac{3}{4}; 0, \frac{1}{2}, \frac{3}{4} \quad (\text{VI-7})$$

The remaining atoms are in the positions given by Eq. (VI-6) and listed in Table VI-3, and the unit cell is sketched on the right-hand side of Fig. VI-5. This structure tends to be unstable relative to its  $\text{K}_2\text{NiF}_4$  counterpart, and is not known to superconduct.

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tetragonal phase, and the metal-to-insulator transition occurs at the tetragonal-to-orthorhombic phase boundary  $x \approx 0.35$  (Matt7, Sleil).

#### D. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller referred to their samples as "metallic, oxygen deficient . . . perovskite like mixed valent copper compounds." Subsequent work has confirmed that the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects.

##### 1. Atom Sizes

In the oxide superconductors Cu replaces the  $Ti^{4+}$  ions ( $0.68 \text{ \AA}$ ) of perovskite, and in most cases retains the  $CuO_2$  layering with two oxygens per copper in the layer. Other cationic replacements tend to be Bi, Ca, La, Sr, Tl, and Y for the larger Ba, forming "layers" containing only one oxygen or none per cation. We see from the following list of ionic radii

|           |                    |        |
|-----------|--------------------|--------|
| $Cu^{2+}$ | $0.72 \text{ \AA}$ |        |
| $Bi^{3+}$ | $0.74 \text{ \AA}$ |        |
| $Y^{3+}$  | $0.94 \text{ \AA}$ |        |
| $Tl^{3+}$ | $0.95 \text{ \AA}$ |        |
| $Bi^{3+}$ | $0.96 \text{ \AA}$ |        |
| $Ca^{2+}$ | $0.99 \text{ \AA}$ | (VI-4) |
| $Sr^{2+}$ | $1.12 \text{ \AA}$ |        |
| $La^{3+}$ | $1.14 \text{ \AA}$ |        |
| $Ba^{2+}$ | $1.34 \text{ \AA}$ |        |
| $O^{2-}$  | $1.32 \text{ \AA}$ |        |

that there are four size groups, with all other cations significantly smaller than the Ba of perovskite. The common feature of  $CuO_2$  layers that are planar or close to planar establishes a fairly uniform lattice size in the  $a, b$  plane. The parameters of the compounds  $LaSrCuO$  ( $a = b = 3.77 \text{ \AA}$ ),  $YBaCuO$  ( $a = 3.83 \text{ \AA}$ ,  $b = 3.89 \text{ \AA}$ ),  $BiSrCaCuO$  ( $a = b = 3.82 \text{ \AA}$ ), and  $TlBaCaCuO$  ( $a = b = 3.86 \text{ \AA}$ ) are all between the ideal fcc oxygen lattice value of  $3.73 \text{ \AA}$  and the perovskite one of  $4.01 \text{ \AA}$ .

Table VI-2 gives the ionic radii of the positively charged ions of various elements of the periodic table. These radii are useful for estimating changes in lattice constant when ionic substitutions are made in existing structures. They also provide some insight into which types of substitutions will be most favorable.

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TABLE VI-2. Ionic Radii in Angstroms of Selected Elements for Various Positive Charge States<sup>a</sup>

| Z   | Element | +1   | +2   | +3   | +4   | +5   | +6   |
|---|---------|------|------|------|------|------|------|
| <i>Alkali</i>                                   |         |      |      |      |      |      |      |
| 3   | Li      | 0.68 |      |      |      |      |      |
| 11  | Na      | 0.97 |      |      |      |      |      |
| 19  | K       | 1.33 |      |      |      |      |      |
| 37  | Rb      | 1.47 |      |      |      |      |      |
| 55  | Cs      | 1.67 |      |      |      |      |      |
| <i>Alkaline earths</i>                          |         |      |      |      |      |      |      |
| 4   | Be      | 0.44 | 0.35 |      |      |      |      |
| 12  | Mg      | 0.82 | 0.66 |      |      |      |      |
| 20  | Ca      | 1.18 | 0.99 |      |      |      |      |
| 38  | Sr      |      | 1.12 |      |      |      |      |
| 56  | Ba      | 1.53 | 1.34 |      |      |      |      |
| <i>Group III</i>                                |         |      |      |      |      |      |      |
| 5   | B       | 0.35 |      | 0.23 |      |      |      |
| 13  | Al      |      |      | 0.51 |      |      |      |
| 31  | Ga      | 0.81 |      | 0.62 |      |      |      |
| 49  | In      |      |      | 0.81 |      |      |      |
| 81  | Tl      | 1.47 |      | 0.95 |      |      |      |
| <i>Group IV</i>                                 |         |      |      |      |      |      |      |
| 6   | C       |      |      |      | 0.16 |      |      |
| 14  | Si      | 0.65 |      |      | 0.42 |      |      |
| 32  | Ge      |      | 0.73 |      | 0.53 |      |      |
| 50  | Sn      |      | 0.93 |      | 0.71 |      |      |
| 82  | Pb      |      | 1.20 |      | 0.84 |      |      |
| <i>Group V</i>                                  |         |      |      |      |      |      |      |
| 15  | P       |      |      | 0.44 |      | 0.35 |      |
| 33  | As      |      |      | 0.58 |      | 0.46 |      |
| 51  | Sb      | 0.89 |      | 0.76 |      | 0.62 |      |
| 83  | Bi      | 0.98 |      | 0.96 |      | 0.74 |      |
| <i>Chalcogenides</i>                            |         |      |      |      |      |      |      |
| 16  | S       |      |      |      | 0.37 |      | 0.30 |
| 34  | Se      | 0.66 |      |      | 0.50 |      | 0.42 |
| 52  | Te      | 0.82 |      |      | 0.70 |      | 0.56 |
| <i>First transition series (3d<sup>n</sup>)</i> |         |      |      |      |      |      |      |
| 21  | Sc      |      |      | 0.81 |      |      |      |
| 22  | Ti      | 0.96 | 0.94 | 0.76 | 0.68 |      |      |
| 23  | V       |      | 0.88 | 0.74 | 0.63 | 0.59 |      |
| 24  | Cr      | 0.81 | 0.89 | 0.63 |      |      | 0.52 |
| 25  | Mn      |      | 0.80 | 0.66 | 0.60 |      |      |

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TABLE VI-2. (continued)

| Z  | Element | +1   | +2   | +3   | +4   | +5   | +6   |
|--|---------|------|------|------|------|------|------|
| 26   | Fe      |      | 0.74 | 0.64 |      |      |      |
| 27   | Co      |      | 0.72 | 0.63 |      |      |      |
| 28   | Ni      |      | 0.69 |      |      |      |      |
| 29   | Cu      | 0.96 | 0.72 |      |      |      |      |
| 30   | Zn      | 0.88 | 0.74 |      |      |      |      |
| <i>Second transition series (4d<sup>n</sup>)</i> |         |      |      |      |      |      |      |
| 39   | Y       |      |      | 0.94 |      |      |      |
| 40   | Zr      | 1.09 |      |      | 0.79 |      |      |
| 41   | Nb      | 1.00 |      |      | 0.74 | 0.69 |      |
| 42   | Mo      | 0.93 |      |      | 0.70 |      | 0.62 |
| 43   | Tc      |      |      |      | 0.67 |      |      |
| 44   | Ru      |      |      | 0.68 |      |      |      |
| 45   | Rh      |      | 0.80 |      | 0.65 |      |      |
| 46   | Pd      |      | 0.89 |      |      |      |      |
| 47   | Ag      | 1.26 | 0.97 |      |      |      |      |
| 48   | Cd      | 1.14 |      |      |      |      |      |
| <i>Third transition series (5d<sup>n</sup>)</i>  |         |      |      |      |      |      |      |
| 72   | Hf      |      |      |      | 0.78 |      |      |
| 73   | Ta      |      |      |      |      | 0.68 |      |
| 74   | W       |      |      |      | 0.70 |      | 0.62 |
| 75   | Re      |      |      |      | 0.72 |      |      |
| 76   | Os      |      |      |      | 0.88 |      | 0.69 |
| 77   | Ir      |      |      |      | 0.68 |      |      |
| 78   | Pt      |      | 0.80 |      | 0.65 |      |      |
| 79   | Au      | 1.37 |      | 0.85 |      |      |      |
| 80   | Hg      | 1.27 | 1.10 |      |      |      |      |
| <i>Rare earths (4f<sup>n</sup>)</i>              |         |      |      |      |      |      |      |
| 57   | La      | 1.39 |      | 1.14 |      |      |      |
| 58   | Ce      | 1.27 |      | 1.07 | 0.94 |      |      |
| 59   | Pr      |      |      | 1.06 | 0.92 |      |      |
| 60   | Nd      |      |      | 1.04 |      |      |      |
| 61   | Pm      |      |      | 1.06 |      |      |      |
| 62   | Sm      |      |      | 1.00 |      |      |      |
| 63   | Eu      |      |      | 0.98 |      |      |      |
| 64   | Gd      |      |      | 0.62 |      |      |      |
| 65   | Tb      |      |      | 0.93 | 0.81 |      |      |
| 66   | Dy      |      |      | 0.92 |      |      |      |
| 67   | Ho      |      |      | 0.91 |      |      |      |
| 68   | Er      |      |      | 0.89 |      |      |      |
| 69   | Tm      |      |      | 0.87 |      |      |      |
| 70   | Yb      |      |      | 0.86 |      |      |      |
| 71   | Lu      |      |      | 0.85 |      |      |      |

\*Three anion radii are 1.32 for O<sup>2-</sup>, 1.33 for F<sup>-</sup>, and 1.84 for S<sup>2-</sup> (*Handbook of Chemistry and Physics*).

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## 2. Unit Cell Stacking

Three and four fundamental fcc unit cells stack vertically to form the superconducting unit cells of YBaCuO and LaSrCuO, respectively, with some oxygens removed in the process. This causes the vertical height or  $c$  parameter of the unit cell to be less than that expected for the stacking of perovskite cells:

$$\begin{aligned} \text{YBaCuO: } c &\approx 11.7 \text{ \AA}, 3c_{\text{fcc}} = 11.19 \text{ \AA}, 3c_{\text{per}} = 12.03 \text{ \AA} \\ \text{LaSrCuO: } c &\approx 13.18 \text{ \AA}, 4c_{\text{fcc}} = 14.92 \text{ \AA}, 4c_{\text{per}} = 16.04 \text{ \AA} \end{aligned} \quad (\text{VI-5})$$

Similar stackings occur in the BiSrCaCuO and TlBaCaCuO compounds.

## E. LANTHANUM-COPPER OXIDE

The structure of LaSrCuO,  $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_{4-\delta}$ , called the 21 structure, where M is usually Sr or Ba, is tetragonal in some cases and orthorhombic in others. We will describe the tetragonal case first and then the orthorhombic distortion of it. The structures will be described in terms of the prototype compound  $\text{La}_2\text{CuO}_4$  corresponding to  $x = \delta = 0$  in the above expression, keeping in mind that in the superconducting compounds themselves some of the La atoms are replaced by a divalent cation such as Sr or Ba. Since lanthanum has a charge of +3 and oxygen is -2, it follows that all of the copper is divalent (+2) when  $x = 0$ , and some becomes trivalent for  $x > 0$ .

The compound  $\text{La}_2\text{CuO}_4$  itself is considered to be nonsuperconducting, but some investigators claim that it or portions of it do exhibit superconductivity, perhaps of a filamentary type (Beill, Coop1, Dvora, Gran1, Pick1, Shahe, Skelt, Skel1, Skel2).

### 1. Tetragonal Form

The tetragonal LaSrCuO superconductors crystallize in what is called the  $\text{K}_2\text{NiF}_4$  structure with space group  $I4/mmm$ ,  $D_{4h}^{17}$  and two formula units per unit cell (e.g., Burns, Coll1, Hirot, Mossz, Onoda; Wyck3, p. 68). The copper atoms and one of the oxygen types O(1) are in special positions and the remaining atoms are all in general positions, with a single undetermined parameter associated with the  $z$  coordinate. The positions are

$$\begin{aligned} \text{La} \quad (4e) \quad &0,0,u; 0,0,-u; \frac{1}{2},\frac{1}{2},u+\frac{1}{2}; \frac{1}{2},\frac{1}{2},-u+\frac{1}{2} \\ \text{Cu} \quad (2a) \quad &0,0,0; \frac{1}{2},\frac{1}{2},\frac{1}{2} \\ \text{O}(1) \quad (4c) \quad &0,\frac{1}{2},0; \frac{1}{2},0,0; \frac{1}{2},0,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2} \\ \text{O}(2) \quad (4e) \quad &0,0,v; 0,0,-v; \frac{1}{2},\frac{1}{2},v+\frac{1}{2}; \frac{1}{2},\frac{1}{2},-v+\frac{1}{2} \end{aligned} \quad (\text{VI-6})$$

with  $u = 0.362$  and  $v = 0.182$ . Typical lattice dimensions are  $a = b = 3.77 \text{ \AA}$ ,  $c = 13.18 \text{ \AA}$ . Table VI-3 gives more details on the atom positions and Fig. VI-5a provides a sketch of this 21 structure. Table VI-4 lists the measured lattice

+5 +6

0.69

0.62

0.68

0.62

0.69

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TABLE VI-3. Atom Positions of Regular and Alternate  $\text{La}_2\text{CuO}_4$  Structure, Both of Which Correspond to Space Group  $I4/mmm$ ,  $D_{4h}^{19}$ 

| Complex               | Ideal $z$             | Regular Structure |      |               |               |               | Alternate Structure |      |               |               |               |
|-----------------------|-----------------------|-------------------|------|---------------|---------------|---------------|---------------------|------|---------------|---------------|---------------|
|                       |                       | Atom              | Site | $x$           | $y$           | $z$           | Atom                | Site | $x$           | $y$           | $z$           |
| $\text{CuO}_2$        | 1                     | O(1)              | 4c   | $\frac{1}{2}$ | 0             | 1             | O(1)                | 4c   | $\frac{1}{2}$ | 0             | 1             |
|                       |                       | O(1)              | 4c   | 0             | $\frac{1}{2}$ | 1             | O(1)                | 4c   | 0             | $\frac{1}{2}$ | 1             |
| OLa                   | $\frac{5}{6} = 0.833$ | Cu                | 2a   | 0             | 0             | 1             | Cu                  | 2a   | 0             | 0             | 1             |
|                       |                       | La                | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.862         | La                  | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.862         |
| LaO                   | $\frac{2}{3} = 0.667$ | O(2)              | 4e   | 0             | 0             | 0.818         | O(2)                | 4d   | 0             | $\frac{1}{2}$ | $\frac{3}{4}$ |
|                       |                       | O(2)              | 4e   | 0             | 0             | 0.818         | O(2)                | 4d   | $\frac{1}{2}$ | 0             | $\frac{3}{4}$ |
| $\text{O}_2\text{Cu}$ | $\frac{1}{2}$         | O(2)              | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.682         | La                  | 4e   | 0             | 0             | 0.638         |
|                       |                       | La                | 4e   | 0             | 0             | 0.638         | O(1)                | 4c   | 0             | $\frac{1}{2}$ | $\frac{1}{2}$ |
| LaO                   | $\frac{1}{3} = 0.333$ | O(1)              | 4c   | 0             | $\frac{1}{2}$ | $\frac{1}{2}$ | O(1)                | 4c   | $\frac{1}{2}$ | 0             | $\frac{1}{2}$ |
|                       |                       | O(1)              | 4c   | $\frac{1}{2}$ | 0             | $\frac{1}{2}$ | O(1)                | 4c   | $\frac{1}{2}$ | 0             | $\frac{1}{2}$ |
| OLa                   | $\frac{1}{6} = 0.167$ | Cu                | 2a   | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | Cu                  | 2a   | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |
|                       |                       | La                | 4e   | 0             | 0             | 0.362         | La                  | 4e   | 0             | 0             | 0.362         |
| $\text{CuO}_2$        | 0                     | O(2)              | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.318         | O(2)                | 4d   | $\frac{1}{2}$ | 0             | $\frac{1}{4}$ |
|                       |                       | O(2)              | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.318         | O(2)                | 4d   | 0             | $\frac{1}{2}$ | $\frac{1}{4}$ |
| OLa                   | $\frac{1}{6} = 0.167$ | O(2)              | 4e   | 0             | 0             | 0.182         | La                  | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.138         |
|                       |                       | La                | 4e   | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.138         | O(1)                | 4c   | $\frac{1}{2}$ | 0             | 0             |
| $\text{CuO}_2$        | 0                     | O(1)              | 4c   | $\frac{1}{2}$ | 0             | 0             | O(1)                | 4c   | 0             | $\frac{1}{2}$ | 0             |
|                       |                       | O(1)              | 4c   | 0             | $\frac{1}{2}$ | 0             | O(1)                | 4c   | 0             | $\frac{1}{2}$ | 0             |
| $\text{CuO}_2$        | 0                     | Cu                | 2a   | 0             | 0             | 0             | Cu                  | 2a   | 0             | 0             | 0             |
|                       |                       | Cu                | 2a   | 0             | 0             | 0             | Cu                  | 2a   | 0             | 0             | 0             |

\*Superconducting compounds crystallize in the regular structure (Oguchi; see also Onoda). The ideal  $z$  values in column 2 are for the prototype perovskite.

constants for tetragonal  $\text{LaSrCuO}$  superconductors with various values of  $x$ ,  $y$ , and  $\delta$  in the formula  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_{4-\delta}$ .

## 2. Alternate Tetragonal Form

In the previous section we discussed the tetragonal structure which is adopted by  $\text{LaSrCuO}$  superconductors. It has a variant (Hutir, Oguchi) called the  $\text{Nd}_2\text{CuO}_4$  structure in which the oxygens O(2) are in special sites (4d) instead of the general (4e) sites in the same space group, corresponding to

$$\text{O}(2) \quad (4d) \quad 0, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, 0, \frac{1}{4}; \frac{1}{2}, 0, \frac{3}{4}; 0, \frac{1}{2}, \frac{3}{4} \quad (\text{VI-7})$$

The remaining atoms are in the positions given by Eq. (VI-6) and listed in Table VI-3, and the unit cell is sketched on the right-hand side of Fig. VI-5. This structure tends to be unstable relative to its  $\text{K}_2\text{NiF}_4$  counterpart, and is not known to superconduct.

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structure, Both of

ate Structure

| Site            | x             | y             | z             |
|-----------------|---------------|---------------|---------------|
| La              | $\frac{1}{2}$ | 0             | 1             |
| Cu              | 0             | $\frac{1}{2}$ | 1             |
| O <sub>1</sub>  | 0             | 0             | 1             |
| O <sub>2</sub>  | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.862         |
| O <sub>3</sub>  | 0             | $\frac{1}{2}$ | $\frac{3}{4}$ |
| O <sub>4</sub>  | $\frac{1}{2}$ | 0             | $\frac{3}{4}$ |
| O <sub>5</sub>  | 0             | 0             | 0.638         |
| O <sub>6</sub>  | 0             | $\frac{1}{2}$ | $\frac{1}{2}$ |
| O <sub>7</sub>  | $\frac{1}{2}$ | 0             | $\frac{1}{2}$ |
| O <sub>8</sub>  | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |
| O <sub>9</sub>  | 0             | 0             | 0.362         |
| O <sub>10</sub> | $\frac{1}{2}$ | 0             | $\frac{1}{4}$ |
| O <sub>11</sub> | 0             | $\frac{1}{2}$ | $\frac{1}{4}$ |
| O <sub>12</sub> | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.138         |
| O <sub>13</sub> | $\frac{1}{2}$ | 0             | 0             |
| O <sub>14</sub> | 0             | $\frac{1}{2}$ | 0             |
| O <sub>15</sub> | 0             | 0             | 0             |

also Onoda). The ideal

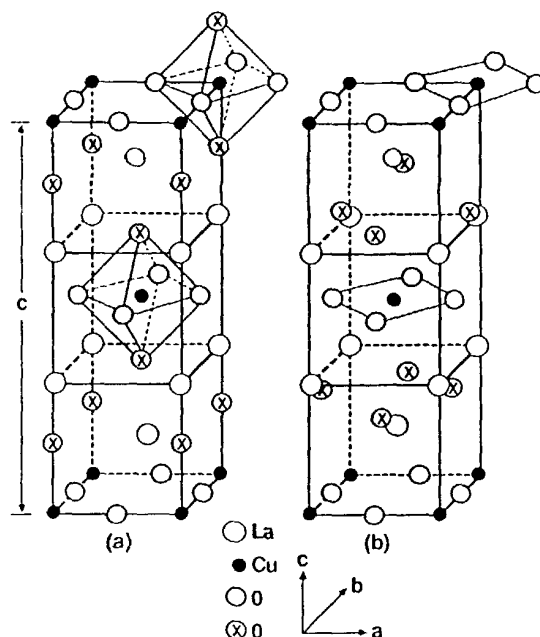


Fig. VI-5. Lanthanum copper oxide tetragonal unit cell. The regular cell (a) associated with the superconducting compounds is shown on the left and the alternative one (b) is on the right (Oguchi; see also Ohba1). The oxygens denoted by  $\otimes$  have different positions in the two cells.

### 3. Orthorhombic Form

The 21 orthorhombic  $\text{LaSrCuO}$  structure (Longo) is related to its tetragonal analogue given by Eq. (VI-6) in the same way that the orthorhombic perovskite structure (VI-3) is related to its tetragonal (VI-2) and cubic (VI-1) forms. This means that the orthorhombic basis directions are at  $45^\circ$  relative to the tetragonal ones, and the number of formula units in the cell is doubled. The situation is similar to that described by Fig. VI-3, with  $a = 5.363 \text{ \AA} = 3.792\sqrt{2} \text{ \AA}$ ,  $b = 5.409 \text{ \AA} = 3.825\sqrt{2} \text{ \AA}$ ,  $c = 13.17 \text{ \AA}$ . Writing the  $a$  and  $b$  lattice parameters times  $\sqrt{2}$  compensates for the new choice of axes and shows that the orthorhombic values are close to the tetragonal  $a = 3.81 \text{ \AA}$  given earlier. There is also very little change in  $c$ . Table VI-5 lists the measured lattice constants for several orthorhombic compounds. The anisotropy factors ANIS

$$\text{ANIS} = \frac{100 |b - a|}{0.5 (b + a)} \quad (\text{VI-8})$$

listed in column 6 give the percentage deviation from tetragonality.

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TABLE VI-4. Selected Lattice Parameters for  $(R_{1-x}M_x)_2CuO_{4-\delta}$  Type Superconductors with Tetragonal Structure<sup>a</sup>

| R-M   | x     | Lattice Parameters <sup>b</sup> |         | Ref.  |
|-------|-------|---------------------------------|---------|-------|
|       |       | a = b (Å)                       | c (Å)   |       |
| Y-Ba  | 0.4   | 3.828                           | 12.68   | Allge |
| La-Ba | 0.05  | 3.782                           | 13.168  | Skelt |
|       | 0.075 | 3.7817                          | 13.2487 | Yuzzz |
|       | 0.075 | 3.787                           | 13.31   | Fujit |
|       | 0.1   | 3.791                           | 13.35   | Fujit |
| La-Sr | 0.05  | 3.7839                          | 13.211  | Tara1 |
|       | 0.05  | 3.78                            | 13.25   | Hidak |
|       | 0.063 | 3.7784                          | 13.216  | Tara1 |
|       | 0.075 | 3.7793                          | 13.2    | Decro |
|       | 0.075 | 3.7771                          | 13.226  | Tara1 |
|       | 0.075 | 3.776                           | 13.234  | Shelt |
|       | 0.075 | 3.772                           | 13.247  | Brunz |
|       | 0.087 | 3.7739                          | 13.232  | Tara1 |
|       | 0.1   | 3.7739                          | 13.23   | Tara1 |
|       | 0.1   | 3.777                           | 13.2309 | Przys |
|       | 0.112 | 3.7708                          | 13.242  | Tara1 |
|       | 0.125 | 3.7685                          | 13.247  | Tara1 |
|       | 0.132 | 3.7666                          | 13.255  | Tara1 |
|       | 0.15  | 3.7657                          | 13.259  | Tara1 |

<sup>a</sup>The table is sorted by cations and then by increasing x, the dopant parameter (prepared by M. M. Rigney).

<sup>b</sup>The a and b lattice parameters were converted from measured values of  $a_0$ ,  $b_0$  of Fig. VI-3 through the expression  $a = a_0/\sqrt{2}$ ,  $b = b_0/\sqrt{2}$ .

Copper atoms and one of the oxygen types O(1) are in special positions; the remaining two atoms La and O(2) are in general positions with a single undetermined parameter associated with the z coordinate. The space group is  $Fmmm$ ,  $D_{2h}^{22}$ , and the positions of the atoms are as follows:

$$\begin{array}{ll}
 \text{La} & (8i) \quad 0,0,u; 0,\frac{1}{2},\frac{1}{2}+u; \frac{1}{2},0,\frac{1}{2}+u; \frac{1}{2},\frac{1}{2},u; \\
 & \quad 0,0,-u; 0,\frac{1}{2},\frac{1}{2}-u; \frac{1}{2},0,\frac{1}{2}-u; \frac{1}{2},\frac{1}{2},-u \\
 \text{Cu} & (4a) \quad 0,0,0; 0,\frac{1}{2},\frac{1}{2}; \frac{1}{2},0,\frac{1}{2}; \frac{1}{2},\frac{1}{2},0 \\
 \text{O(1)} & (8e) \quad \frac{1}{4},\frac{1}{4},0; \frac{1}{4},\frac{3}{4},\frac{1}{2}; \frac{3}{4},\frac{1}{4},\frac{1}{2}; \frac{3}{4},\frac{3}{4},0 \\
 & \quad \frac{1}{4},\frac{1}{4},\frac{1}{2}; \frac{1}{4},\frac{3}{4},0; \frac{3}{4},\frac{1}{4},0; \frac{3}{4},\frac{3}{4},\frac{1}{2} \\
 \text{O(2)} & (8i) \quad 0,0,v; \dots \text{ (same as La with } v \text{ replacing } u \text{)}
 \end{array} \quad (VI-9)$$

where the parameters  $u = 0.362$  and  $v = 0.182$  have the same values as in the tetragonal case presented above. Since  $u$  and  $v$  are the same and the lattice constants are so close to the tetragonal values, the sketch of the tetragonal unit cell in Fig. VI-5a applies here also. Another work (Hiro, see also Onoda) assigned

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TABLE VI-5. Selected Lattice Parameters for  $(R_{1-x}M_x)_2CuO_{4-\delta}$  Type Superconductors with the Orthorhombic Structure<sup>a</sup>

| R-M   | x     | Lattice Parameters |        |        | ANIS | Ref.  |
|-------|-------|--------------------|--------|--------|------|-------|
|       |       | a (Å)              | b (Å)  | c (Å)  |      |       |
| La-Ba | 0.02  | 3.786              | 3.811  | 13.17  | 0.66 | Fujit |
|       | 0.075 | 3.786*             | 3.808* | 13.257 | 0.58 | Shelt |
|       | 0.075 | 3.798*             | 3.803* | 13.234 | 0.13 | Onoda |
| La-Ba | 0.1   | 3.786*             | 3.824* | 13.264 | 1.00 | Hiroi |
| La-Ca | 0.075 | 3.772*             | 3.808* | 13.168 | 0.95 | Shelt |

<sup>a</sup>ANIS is the anisotropy factor  $100|b - a|/0.5(b + a)$  (prepared by M. M. Rigney).<sup>b</sup>The a and b lattice parameters were converted from the measured values of  $a_0$ ,  $b_0$  of Fig. VI-3 through the expressions  $a = a_0/\sqrt{2}$ ,  $b = b_0/\sqrt{2}$ .

$(La_{0.9}Ba_{0.1})_2O_4$  to the space group  $Pccm$ ,  $D_{2h}^3$  with  $a = 5.354 = 3.786\sqrt{2}$  Å,  $b = 5.408 = 3.824\sqrt{2}$  Å, and  $c = 13.264$  Å.

#### 4. Phase Transition

The compounds  $(La_{1-x}M_x)_2CuO_4$  with  $M = Sr$  and  $Ba$  are orthorhombic at low temperatures and low M contents, and tetragonal otherwise, and superconductivity has been found on both sides of this transition (Baris, Bedn3, Birge, Dayzz, Dvora, Fujit, Gree1, Kangz, Koyam, Mihal, Paulz; see also Heldz). The prototype compound  $La_2CuO_4$  itself also exhibits the tetragonal-to-orthorhombic transition. The phase diagram of Fig. VI-6 shows the tetragonal, orthorhom-

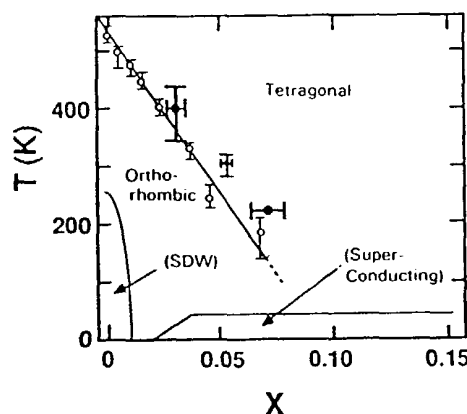


Fig. VI-6. Phase diagram showing data points along the tetragonal-to-orthorhombic transition line for  $(La_{1-x}Ba_x)_2CuO_{4-\delta}$  (○, Fujit) and  $(La_{1-x}Sr_x)_2CuO_4$  (●, Moret). The spin-density wave (SDW) and superconducting regions are indicated. These two compounds have about the same superconducting region.

bic, superconducting, and spin-density wave (SDW) regions for the barium compound (Fujit), and data points for the strontium compound (Moret, More8). An alternate phase diagram has been proposed (Ahar1). Alkaline metal contents much larger than those shown on the figure (e.g.,  $x \approx 0.5$ ) can be non-superconducting. The SDW region occurs below the minimum concentration for the onset of superconductivity. Another work (Geise) showed that LaSr(0.04) undergoes a structural phase transition between 180 and 300 K.

### 5. Generation of LaSrCuO Structures

The LaSrCuO tetragonal structures may be visualized as being derived from four LaCuO<sub>3</sub> perovskite unit cells of the type illustrated in Fig. VI-1 stacked one above the other along the  $z$  or  $c$  axis. To generate La<sub>2</sub>CuO<sub>4</sub> in the K<sub>2</sub>NiF<sub>4</sub> structure the layers of CuO<sub>2</sub> atoms on the  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$  levels of this four-cell stacking are removed, La and O are interchanged on two other layers, and the middle layer Cu atom is shifted from the edge to the center point ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) of the unit cell. Then the cell is compressed vertically from 14.9 to 13.2 Å (Table VI-4) to take up the space formerly occupied by the removed CuO<sub>2</sub> layers. Finally, the lanthanums along the  $c$  axis and the oxygens along the side edges are shifted vertically to accommodate the new atom arrangement.

To generate La<sub>2</sub>CuO<sub>4</sub> with the Nd<sub>2</sub>CuO<sub>4</sub> arrangement from this same four-cell stacking all of the oxygens on the vertical edges are removed, and two lanthanums are moved to edge sites. Copper is handled the same way as before, so in both cases the generated structure lacks two CuO<sub>2</sub> layers.

### 6. Layering Scheme of LaSrCuO

When we described the LaSrCuO structures we left out what is perhaps their most important characteristic, namely, their layered aspect. Lanthanum copper oxide may be looked upon as consisting of Cu-O layers of square-planar coordinated copper ions with lanthanum and O(2)-type oxygen ions populating the spaces between the layers. These Cu-O layers are stacked equally spaced, perpendicular to the  $c$  axis, as shown in Fig. VI-7, and their oxygens are aligned along the  $c$  axis, as indicated by the vertical dotted line on the left side of the figure. The copper ions, on the other hand, are not aligned vertically, but rather alternate between (000) and ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) sites in adjacent layers, as illustrated in Figs. VI-5 and VI-7.

The copper is actually octahedrally coordinated with oxygen, but the Cu-O distance of 1.9 Å in the CuO<sub>2</sub> planes is much less than the vertical distance of 2.4 Å between copper and the oxygens above and below, as shown in Fig. VI-8. When the structure is distorted orthorhombically the Cu-O spacings in both the planes and the  $c$  direction remain quite close to their tetragonal counterparts.

The copper ions and the O(1)-type oxygens in the planes are both in special sites in the tetragonal and orthorhombic forms, in accordance with Eqs. (VI-6) and (VI-9), and as a result the plane is perfectly flat in both cases. When the

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## FACSIMILE

DATE: Dec. 10, 1998 NO. OF PAGES TO FOLLOW: 28

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 10, 1998

Serial No. 08/303,561

Group Art Unit: 1105

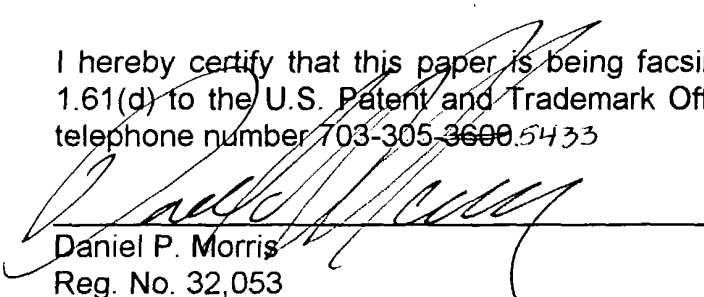
Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

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**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

## IN THE CLAIMS

115. (Amended) A method comprising the steps of:

forming a composition including copper, oxygen and [any] an  
element selected from the group consisting of at least one  
Group II A element and at least one element selected from

the group consisting of a rare earth element and a Group  
III B element, where said composition is a mixed copper

oxide having a non-stoichiometric amount of oxygen therein  
and exhibiting a superconducting state at a temperature greater  
than 26°K;

maintaining said composition in said superconducting state at a  
temperature greater than 26°K; and

passing an electrical current through said composition while  
said composition is in said superconducting state.

120. (Amended) A method comprising the steps of:

forming a composition including a transition metal, oxygen and [any] an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed transitional metal oxide formed from said transition metal and said oxygen, said mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

123. (Amended) A superconductive method for conducting an electric current

essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $[T] T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and



(c) causing an electric current to flow in the superconductor element.

129. (Amended) A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition [while] with said phase exhibiting said superconductivity.

130. (Amended). A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide [being] at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

131. (Amended). A method comprising providing a superconducting copper oxide having a superconductive onset temperature greater than 26°K, [maintaing] maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current [therein] in said superconducting oxide.

132. (Amended) . A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a [superconduting] superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

133. (Amended). A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, [maintianing] maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

134. (Amended) A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than 26°K and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

135. (Amended) A method comprising flowing a superconducting electrical current in a copper oxide having a  $T_c$  greater than 26°K and maintaining said copper oxide at a temperature less than said  $T_c$ .

137. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a III B element, an alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

138. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, alkaline earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

139. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

140. (Amended) A method comprising flowing a superconducting electrical current in a composition of matter having a  $T_c$  greater than 26°K carrying, said composition comprising at least one each of a III B element, and copper oxide and maintaining said composition of matter at a temperature less than said  $T_c$ .

141. (Amended) A method comprising flowing a superconducting electrical current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said transition metal oxide at a temperature less than said  $T_c$ .

142. (Amended) A method comprising flowing a superconducting electrical current in a copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$  and maintaining said copper oxide composition of matter at a temperature less than said [TC]  $T_c$ .

Added claims:

143. (Added) A method, comprising the steps of:

forming a composition including a transition metal, a group IIIB element, an alkaline earth element, and oxygen, where said composition is a mixed transition metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K,

maintaining said composition in said superconducting state at a temperature greater than 26°K, and

passing an electrical current through said composition while said composition is in said superconducting state.

144. (Added) The method of claim 143, where said transition metal is copper.

145. (Added) A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;

(b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

146. (Added) The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.

147. (Added) The superconductive method according to claim 146 in which the rare-earth or rare-earth-like element is lanthanum.

148. (added) The superconductive method according to claim 146 in which the alkaline-earth element is barium.

149. (Added) The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

150. (Added) The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

151. (Added) The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

152. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:  
(a) providing a superconductor element made of a superconductive composition, the superconductive composition

consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

153. (Added) The superconductive method according to claim 103 in which said at least one element is lanthanum.

154. (Added) The superconductive method according to claim 152 in



which the alkaline-earth element is barium.

155. (Added) The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

156. (Added) The superconductive method according to claim 155 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

157. (Added) The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

158. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive

composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element, and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

159. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide

compound including at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

160. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite

crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

161. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting

of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

162. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive

transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

163. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a substantially layered perovskite crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and

a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

164. (Added) A method according to claim 129 wherein said composition comprises a substantially layered perovskite crystal structure.

165. (Added) A method according to claim 130 wherein said superconducting transistor metal oxide comprises a substantially layered perovskite crystal structure.

166. (Added) A method according to claim 131 wherein said  
superconducting copper oxide comprises a substantially layered  
perovskite crystal structure.
167. (Added) A method according to claim 132 wherein said  
superconducting oxide composition comprises a substantially layered  
perovskite crystal structure.
168. (Added) A method according to claim 133 wherein said  
superconducting oxide composition comprises a substantially layered  
perovskite crystal structure.
169. (Added) A method according to claim 134 wherein said transistor  
metal oxide comprises a substantially layered perovskite crystal  
structure.
170. (Added) A method according to claim 135 wherein said copper oxide  
comprises a substantially layered perovskite crystal structure.
171. (Added) A method according to claim 136 wherein said composition  
comprises a substantially layered perovskite crystal structure.



172. (Added) A method according to claim 137 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

173. (Added) A method according to claim 138 wherein said composition of matter comprises substantially layered perovskite crystal structure.

174. (Added) A method according to claim 139 wherein said composition of matter comprises a substantially layered perovskite crystal structure.

175. (Added) A method according to claim 140 wherein said composition of matter comprises substantially layered perovskite crystal structure.

176. (Added) A method according to claim 141 wherein said transistor metal oxide comprises substantially layered perovskite crystal structure.

177. (Added) A method according to claim 142 wherein said copper oxide composition comprises substantially layered perovskite crystal structure.

#### **REMARKS**

Reconsideration is respectfully requested in view of and changes to the claims and the remarks herein. Please contact the undersigned to conduct a telephone

interview in accordance with MPEP 713.01 to resolve any remaining requirements and/or issues prior to sending another Office Action. Relevant portions of MPEP 713.01 are included on the signature page of this amendment. In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to *reconsider* the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

In paragraphs 6-7 on pages 12 -16 of the referenced office action Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135 and 137-142 have been rejected under 35 USC 112. All changes suggested by the examiner have been made except for those directed to the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type". These terms occur in claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123. Added claims 143 to 163 have there same wording as these claims and include the changes suggested by the examiner to overcome the rejection based on these terms. As stated by applicants in previous responses these are terms of art and well understood by persons of skill in the art.

Claims 164-177 are added, support found throughout the specification and claims.

In paragraph 5 of the referenced office action claims 129-131, 134, 135, 139-142 added by applicants in there response dated April 27, 1998 have been rejected under 35 USC 112 as not enabled. Applicants respectfully disagree. The examiner has given no specific reason why these claims are not enabled.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

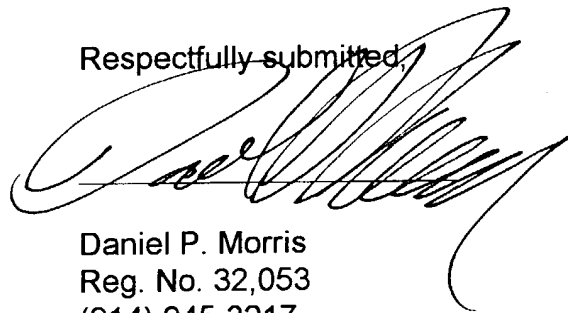
If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', is written over a horizontal line.

Daniel P. Morris  
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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 3, 1998

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

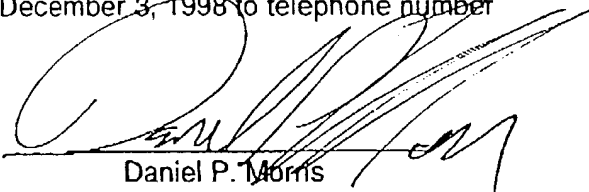
Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATE OF FACSIMILE TRANSMISSION**

I hereby certify that this paper is being facsimile transmitted under 37 CFR 1.61(d) to the U.S. Patent and Trademark Office on December 3, 1998 to telephone number 703-305-5433.



Daniel P. Morris  
Reg. No. 32,053

**Petition for Withdrawal of the Final Rejection  
dated June 25, 1998**

Applicants petition for withdrawal of the final rejection rejection dated June 25, 1998  
for the following reasons:

Claims 24-26, 86-90, 96-135 and 137-142 have been rejected under 35 USC 102 (a) as anticipated by the Asahi Shinbum article and have been rejected under 35 USC 103 as being unpatentable over the Asahi Shinbum article. Applicants have disagreed for various reasons of record. One of those reasons is that applicants have proven that

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 3, 1998

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

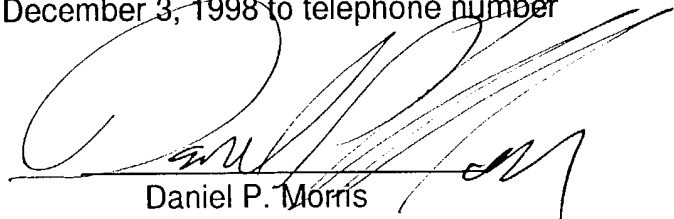
Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
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the conception of their invention was in the United states prior to the date of the Asahi Shinbum article , November 28, 1986, and applicants have proven that they were diligent from prior to the date of the Asahi Shinbum article by instructing coworkers in the United States until December 3, 1986 which is the date the examiner believes is the earliest date of applicants reduction to practice in the United States. (For the reasons of record applicants believe that they have shown that their invention was reduced to practice in the United States prior to the date of the Asahi Shinbum article). The examiner has not rebutted applicants proof that applicants conception was in the United States at their direction prior to the date of the Asahi Shinbum article and the examiner has not denied that applicants have proven that they were diligent by instructing coworkers in the United States from a time prior to the date of the Asahi Shinbum article until the date the examiner believes is the date of applicants' date of reduction to practice in the United States. The details of applicants' proof are discussed at pages 22, line 8 to page 24, last line, of applicant's Substitute Amendment dated March 6, 1997.

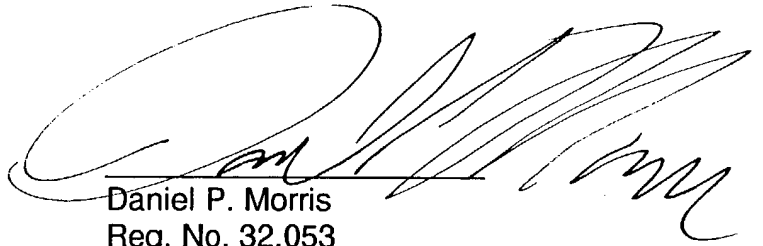
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Willson v. Sherts 81 F 2d 775, 28 USPQ 379 (CCPA 1936) held that an inventor who conceives an invention outside of the United States gets the benefit of the date that a third party, to whom the invention is disclosed, brings the conception into the United States (28 USPQ 379, 381) and that acts in this country done on behalf of the inventors can be used to show diligence to reduction to practice in the United States (28 USPQ 379, 383) . Thus the rejections of applicants' claims under 35 USC 102 and 103 over the Asahi Shinbum article should be withdrawn.

Applicants are entitled to know why the examiner has maintained the rejection under 35 USC 102 and 103 over the Asahi Shinbum article in light of applicants proof which the examiner has not rebutted. Applicants are in the position of having to guess at what are the reasons for maintaining these rejections. Applicants cannot properly appeal these rejections with out knowing the examiner's reasons for maintaining the rejections.

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Respectfully submitted,

A large, stylized handwritten signature in black ink, likely belonging to Daniel P. Morris, is positioned above the printed name and contact information.

Daniel P. Morris  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598



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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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Date: December 3, 1998

Serial No.: 08/303,561

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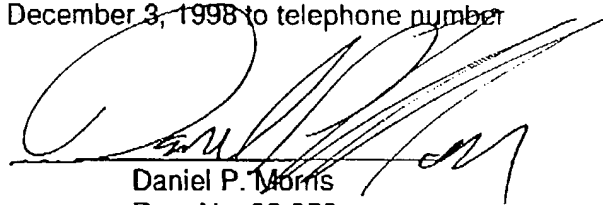
Examiner: M. Kopec

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TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
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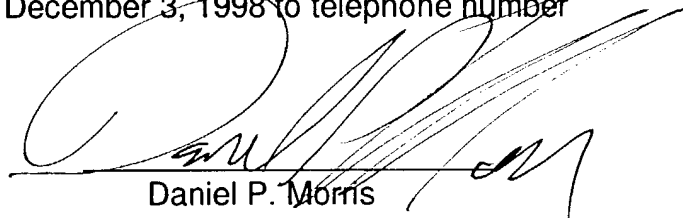
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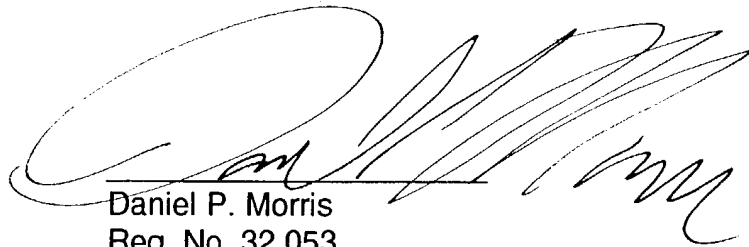
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Respectfully submitted,

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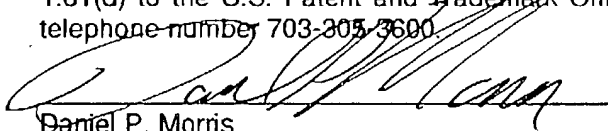
Filed: September 9, 1994  
McGinty

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
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Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**Amendment After Final Rejection**

In response to the final rejection dated June 25, 1998 please consider the  
following:

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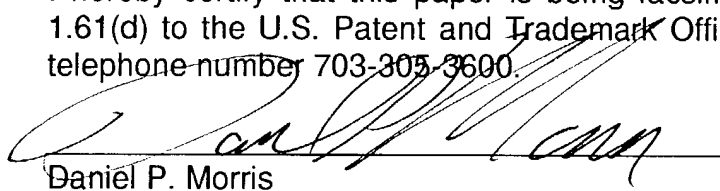
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**Amendment After Final Rejection**

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## IN THE CLAIMS

115.(Amended) A method comprising the steps of:

forming a composition including copper, oxygen and [any] an  
element selected from the group consisting of at least one  
Group II A element and at least one element selected from

the group consisting of a rare earth element and a Group  
III B element, where said composition is a mixed copper

oxide having a non-stoichiometric amount of oxygen therein  
and exhibiting a superconducting state at a temperature greater  
than 26°K;

maintaining said composition in said superconducting state at a  
temperature greater than 26°K; and

passing an electrical current through said composition while  
said composition is in said superconducting state.



120. (Amended) A method comprising the steps of:

forming a composition including a transition metal, oxygen and  
[any] an element selected from the group consisting of at least one  
Group II A element and at least one element selected from the  
group consisting of a rare earth element and a Group III B  
element, where said composition is a mixed transitional metal  
oxide formed from said transition metal and said oxygen, said mixed  
transition metal oxide having a non-stoichiometric amount of oxygen  
therein

and exhibiting a superconducting state at a temperature greater  
than 26°K;

maintaining said composition in said superconducting state  
at a temperature greater than 26°K; and

passing an electrical current through said composition while  
said composition is in said superconducting state.

123.(Amended) A superconductive method for conducting an electric current

essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting

essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $[T] T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

129 (Amended). A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition [while] with said phase exhibiting said superconductivity.

130 (Amended). A method comprising providing a superconducting transition

metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide [being] at a temperature less than

said superconducting onset temperature and flowing a superconducting current therein.

131 (Amended). A method comprising providing a superconducting copper oxide having a superconductive onset temperature greater than 26°K, [maintaing] maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current [therein] in said superconducting oxide.

132 (Amended) . A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a [superconduting]

superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

133 (Amended). A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, [maintianing] maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting electrical current therein, said composition comprising at least one each of a Group III B element, an alkaline earth, and copper.

134. (Amended) A method comprising flowing a superconducting electrical current in a transition metal oxide having a  $T_c$  greater than 26°K and maintianing said transition metal oxide at a temperature less than said  $T_c$  .

135. (Amended) A method comprising flowing a superconducting electrical current in a copper oxide having a  $T_c$  greater than 26°K and maintaining said copper oxide at a temperature less than said  $T_c$ .

136. (Amended) A method comprising the steps of:

forming a composition of the formula  $Ba_xLa_{x-5}Cu_{50}Y$ , wherein

x is from about 0.75 to about 1 and y is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical current through said composition while said metal oxide phase is in said superconducting state.

137. (Amended) A method comprising flowing a superconducting electrical current

in a composition of matter having a  $T_c$  greater than 26°K,  
said composition comprising at least one each of a III B  
element, an alkaline earth, and copper oxide and maintaining said  
composition of matter at a temperature less than said  $T_c$ .

138. (Amended) A method comprising flowing a superconducting electrical current

in a composition of matter having a  $T_c$  greater than 26°K,  
said composition comprising at least one each of a rare  
earth, alkaline earth, and copper oxide and maintaining said  
composition of matter at a temperature less than said  $T_c$ .

139. (Amended) A method comprising flowing a superconducting electrical current

in a composition of matter having a  $T_c$  greater than 26°K,  
said composition comprising at least one each of a rare

earth, and copper oxide and maintaining said composition of matter at  
a        temperature less than said  $T_c$ .

140. (Amended) A method comprising flowing a superconducting electrical  
current in a        composition of matter having a  $T_c$  greater than 26°K  
carrying, said composition comprising at least one each of  
a III B element, and copper oxide and maintaining said  
composition of matter at a temperature less than said  $T_c$ .

141. (Amended) A method comprising flowing a superconducting electrical  
current  
in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$  and maintaining said  
transition metal oxide at a temperature less than said  $T_c$ .

142. (Amended) A method comprising flowing a superconducting electrical  
current in a        copper oxide composition of matter comprising a  $T_c > 26^\circ\text{K}$   
and maintaining        said copper oxide composition of matter at a  
temperature less than said [TC]         $T_c$ .



Added claims:

143 (Added). A method, comprising the steps of:

forming a composition including a transition metal,  
a [rare earth or rare earth-like] group IIIB element, an  
alkaline earth element, and oxygen, where said  
composition is a mixed transition metal oxide hav-  
ing a non-stoichiometric amount of oxygen therein  
and exhibiting a superconducting state at a tem-  
perature greater than 26°K,

maintaining said composition in said superconducting  
state at a temperature greater than 26°K, and

passing an electrical current through said compo-  
sition while said composition is in said supercon-  
ducting state.

144 (Added). The method of claim 143, where said transition metal  
is copper.

@@@@

- 145 (Added). A superconductive method for causing electric current flow in a superconductive state at a temperature in excess of 26 K, comprising:
- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a [layer-type perovskite-like] substantially layered crystal structure, the composition having a superconductor transition temperature  $T_c$  of greater than 26 K;
  - (b) maintaining the superconductor element at a temperature above 26 K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and
  - (c) causing an electric current to flow in the superconductor element.

146 (Added). The superconductive method according to claim 145 in

which the copper-oxide compound of the superconductive composition includes at least one element selected from the group consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element.

147 (Added). The superconductive method according to claim 146 in which the rare-earth or rare-earth-like element is lanthanum.

148 (added). The superconductive method according to claim 146 in which the alkaline-earth element is barium.

149 (Added). The superconductive method according to claim 145 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

150 (Added). The superconductive method according to claim 149 in which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

151 (Added). The superconductive method according to claim 150 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

152 (Added). A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition

consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group

consisting of a rare-earth element and a Group III B element and at least one alkaline-earth element, the

composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an

effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26 K;

- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

153 (Added). The superconductive method according to claim 103 in which said at least one element is lanthanum.

154 (Added). The superconductive method according to claim 152 in which the alkaline-earth element is barium.

155(Added). The superconductive method according to claim 152 in which the copper-oxide compound of the superconductive composition includes mixed valent copper ions.

156 (Added). The superconductive method according to claim 155 in

which the copper-oxide compound includes at least one element in a nonstoichiometric atomic proportion.

157 (Added). The superconductive method according to claim 156 in which oxygen is present in the copper-oxide compound in a nonstoichiometric atomic proportion.

158 (Added). A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element; and a Group III B element;

(b) maintaining the superconductor element at a temperature

above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

159 (Added).. A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of

a Group II A element, a rare earth element and a Group

III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower

limit defined by an effectively-zero-bulk-resistivity

intercept temperature  $T_{p=0}$ , the transition-onset

temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature

below the effectively-zero-bulk-resistivity intercept

temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

160 (Added). A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group



consisting of a rare earth element and a Group III B element;

1

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

161 (Added). A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a substantially layered perovskite crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive-resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit

defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

162 (Added). A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a substantially layered perovskite crystal structure, the composition having a superconductive transition

temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from

the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

163 (Added). A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a substantially layered

perovskite crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element

selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

#### **REMARKS**

Reconsideration is respectfully requested in view of and changes to the claims and the remarks herein. Please contact the undersigned to conduct a telephone interview in accordance with MPEP 713.01 to resolve any remaining requirements and/or issues prior to sending another Office Action. Relevant portions of MPEP 713.01 are included on the signature page of this amendment. In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the

Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

In paragraphs 6-7 on pages 12 -16 of the referenced office action Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135 and 137-142 have been rejected under 35 USC 112. All changes suggested by the examiner have been made except for those directed to the terms "layer-like", "perovskite-like", "rare-earth-like", and "layer-type". These terms occur in claims 86-87, 96-108, 112, 113, 117, 118, 122, and 123. Added claims 143 to 163 have there same wording as these claims and include the changes suggested by the examiner to overcome the rejection based on these terms. As stated by applicants in previous responses these are terms of art and well understood by persons of skill in the art.

In paragraph 5 of the referenced office action claims 129-131, 134, 135, 139-142 added by applicants in there response dated April 27, 1998 have been rejected under 35 USC 112 as not enabled. Applicants respectfully disagree. The examiner has given no specific reason why these claims are not enabled.

The examiner has rejected all pending claims, except for claim 136 which is allowable, under 35 USC 102 as anticipated by the Asahi Shinbum article. In the prior response applicants have proven that the conception of applicants' invention was in this country prior to the date of the Asahi Shinbum article and that they were diligent from that time until the actual reduction to practice in this country. Thus applicants have effectively sworn behind the date of the Asahi Shinbum article. The examiner has ignored this stating at page 19 of the office action in paragraph d. ii "Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference." This comment is inconsistent with the law. The examiner is being arbitrary and capacious in not responding to applicants'

arguments. This is clearly erroneous. Applicants have sworn behind the date of the Asahi Shinbum article and have thus over come the rejection of the claims as anticipated by the Asahi Shinbum article and withdrawal of this rejection is respectfully requested. The examiner is placing applicants in a position of having to guess why in the apparent view of the examiner they have not effectively sworn behind the date of the Asahi Shinbum article. Thus applicants can not properly appeal this rejection since the examiner has not stated a coherent rejection. In view thereof applicant respectfully request that the final rejection be withdrawn so that applicants can be informed of the reason why the examiner apparently believes that applicants have not effectively sworn behind the date of the Asahi Shinbum article by the combination of affidavits under 37 CFR 1.132 which prove that the conception of applicants' invention was in this country prior to the date of the Asahi Shinbum article and that they were diligent from that time until the actual reduction to practice in this country.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

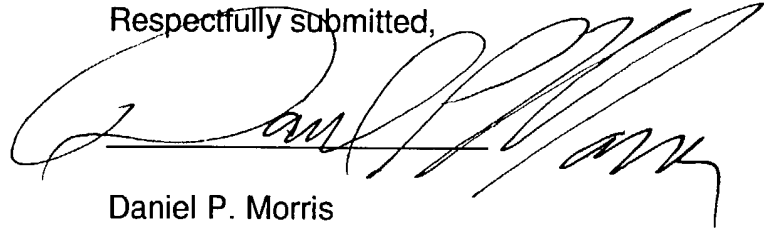
If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

In the event that this amendment does not result in allowance of all such claims, the undersigned attorney respectfully requests a telephone interview at the Examiner's earliest convenience.

MPEP 713.01 states in part as follows:

Where the response to a first complete action includes a request for an interview or a telephone consultation to be initiated by the examiner, ... the examiner, as soon as he or she has considered the effect of the response, should grant such request if it appears that the interview or consultation would result in expediting the case to a final action.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Daniel P. Morris', written over a horizontal line.

Daniel P. Morris  
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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. |
|-----------------|-------------|----------------------|---------------------|
| 08/383,561      | 09/09/94    | BEDNORZ              | Y0987074BY          |

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IM51/0625

EXAMINER  
MC GINTY, D

ART UNIT  
1751

PAPER NUMBER

DATE MAILED: 06/25/98

*DUE 9/25/98*  
*FINAL*

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

IBM CORPORATION  
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DEPARTMENT



# Office Action Summary

Application No.  
**08/303,561**

Applicant(s)  
**Bednorz et al.**

Examiner  
**Douglas J. McGinty**

Group Art Unit  
**1751**



☒ Responsive to communication(s) filed on May 1, 1998 and May 14, 1998

☒ This action is **FINAL**.

☐ Since this application is in condition for allowance except for formal matters, **prosecution as to the merits is closed** in accordance with the practice under *Ex parte Quayle* 35 C.D. 11; 453 O.G. 213.

A shortened statutory period for response to this action is set to expire 3 month(s), or thirty days, whichever is longer, from the mailing date of this communication. Failure to respond within the period for response will cause the application to become abandoned. (35 U.S.C. § 133). Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

## Disposition of Claim

☒ Claim(s) 24-26, 86-90, and 96-142 is/are pending in the application

Of the above, claim(s) \_\_\_\_\_ is/are withdrawn from consideration

☒ Claim(s) 136 is/are allowed.

☒ Claim(s) 24-26, 86-90, 96-135, and 137-142 is/are rejected.

☐ Claim(s) \_\_\_\_\_ is/are objected to.

☐ Claims \_\_\_\_\_ are subject to restriction or election requirement.

## Application Papers

☐ See the attached Notice of Draftsperson's Patent Drawing Review, PTO-948.

☐ The drawing(s) filed on \_\_\_\_\_ is/are objected to by the Examiner.

☐ The proposed drawing correction, filed on \_\_\_\_\_ is ☐ approved ☐ disapproved.

☐ The specification is objected to by the Examiner.

☐ The oath or declaration is objected to by the Examiner.

## Priority under 35 U.S.C. § 119

☒ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☒ All ☐ Some\* ☒ None of the CERTIFIED copies of the priority documents have been  
☐ received.

☒ received in Application No. (Series Code/Serial Number) 08/053,307.

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

\*Certified copies not received: \_\_\_\_\_

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

## Attachment(s)

☐ Notice of References Cited, PTO-892

☐ Information Disclosure Statement(s), PTO-1449, Paper No(s). \_\_\_\_\_

☐ Interview Summary, PTO-413

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

— SEE OFFICE ACTION ON THE FOLLOWING PAGES —

### DETAILED ACTION

1. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action. The rejections and objections, if any, from the previous Office Action have been withdrawn if not repeated in this Office Action.

2. It is requested that this Examiner be notified of all pending, related applications.<sup>1</sup> That notice need not be in a PTO form - 1449, however.<sup>2</sup>

#### *Status of the Claims*

3. Claims 24-26, 86-90, and 96-142 are pending.

#### *Priority*

4. Acknowledgment is made of applicant's claim for priority under 35 U.S.C. § 119. The certified copy has been filed in parent application, Serial No. 08/053,307, filed on April 23, 1993 as paper no. 28.

a. However, a review of that certified copy, which is in English, indicates that it does not support the present assertion of priority. Support is not found in that certified copy for the invention as presently claimed. See MPEP 201.13 et seq. and 201.14 et seq.

b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The applicants quote some passages out of the priority document and argue that the present claims are fully based that document. Nevertheless, that priority document is not deemed to provide basis for the following limitations found in the present claims:

i. The limitations "a composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen", as found in claim 86 (lines 2-4). The certified priority document may provide basis for the formula  $RE_2TM.O_4$  at p. 2, para. 4, but the claimed composition is deemed to be much broader than that formula.

---

<sup>1</sup> See MPEP 2001.06(b).

<sup>2</sup>See MPEP 901.03.

ii. The limitation "non-stoichiometric amount of oxygen", as found in claim 86 (line 6). Basis may be seen for an oxygen deficit at p. 2, para. 4, but no such basis is seen for the more general limitation of "a nonstoichiometric amount of oxygen".

iii. The limitation "a composition exhibiting a superconductive state", as found in claim 88 (line 2), wherein the composition is a "(transition) metal oxide", as found in claims 24 (lines 1 and 2), 89 and 90. The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but "a composition", "metal oxide", or "transition metal oxide" is deemed to be much broader than the formula  $RE_2TM.O_4$ .

iv. The limitation "a copper-oxide compound", as recited in claim 96 (line 6). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but "a copper-oxide compound" is not deemed to be equivalent to a composition of the formula  $RE_2TM.O_4$ . Basis is not seen in the certified priority document for "a copper-oxide compound" with the breadth of the present claims.

v. The limitation to the effect that "the copper oxide compound includes (including) at least one rare-earth or rare-earth-like element and at least one alkaline-earth element", as recited in claim 97 (lines 3 and 4) and claim 103 (lines 6-8). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but basis is not seen for the more general limitation of "a copper-oxide compound" with a rare-earth (like) element and an alkaline earth element.

vi. The limitation to the effect that "the copper-oxide compound includes at least one element (oxygen) in a nonstoichiometric atomic proportion", as found in claim 101 (lines 2 and 3), 102 (lines 2 and 3), 107 (lines 2 and 3), and 108 (lines 2 and 3). Basis may be seen for an oxygen deficit as discussed above, but no such basis is seen for the more general limitation of "a nonstoichiometric atomic proportion".

vii. The limitation as to "the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ ", as found in claim 103 (lines 13, 16, and 17). The critical temperature,  $T_c$ , is discussed throughout that certified priority document, but not  $T_{p=0}$ .

c. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but not found to be persuasive.

i. The applicants quote portions out of the priority document and assert that those quoted sections "clearly (support) a much broader composition than the Examiner is claiming it does, and that the priority document, in fact, does support applicant's (sic) claim 86." The fact remains, nevertheless, that the priority document refers to the general formula  $RE_2TM.O_4$  in which the rare earth element (RE) may be partially substituted with a Group IIA metal. That disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to that general formula.

ii. The applicants argue that the disclosure of varying amounts of oxygen in the priority document provides support for earlier priority for the term "non-stoichiometric amount of oxygen". Again, however, that disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to those varying amounts.

iii. The applicants urge that the disclosure in the priority document of the formula  $RE_2TM.O_4$  provides support for their limitations of "transition metal", "copper-oxide compounds", "rare earth or rare earth-like elements", and "alkaline earth element". Again, however, that disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to that formula.

iv. The applicants further "assume that the Examiner agrees with applicant's (sic) statements in their prior response in that the concept of the intercept temperature is well known in the prior art and can be included in claim 103." No basis is seen for that assumption. As noted in the previous Office Action and repeated above, the term " $T_{p=0}$ " is not found in the priority document. Well known or not, there is no basis for that term in the priority document.

d. Applicants' arguments filed May 1, 1998 (#64) and May 14, 1998 (#62) have been fully considered but not found to be persuasive. The applicants' arguments have been fully discussed above.

*Claim Rejections - 35 USC § 112*

**5. The specification is objected to under 35 U.S.C. § 112, *first paragraph*, as failing to provide an enabling disclosure commensurate with the scope of the claims.**

a. The present specification is deemed to be enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_y$ . The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases.<sup>3</sup> Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112.<sup>4</sup> Merely reciting a desired result does not overcome this failure.<sup>5</sup> In particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?

b. It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion".<sup>6</sup>

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<sup>3</sup>See In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218. See also, In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977) (J. Rich).

<sup>4</sup>See In re Cook, 169 USPQ 298, 302; and Cosden Oil v. American Hoechst, 214 USPQ 244, 262.

<sup>5</sup>See In re Corkill, 226 USPQ 105, 1009.

<sup>6</sup>See Brenner v. Manson, 383 US 519, 148 USPQ 689.

c. **Claims 24-26, 86-90, 96-113, 129-131, 134, 135, and 139-142 are rejected under 35 U.S.C. § 112, *first paragraph*, for the reasons set forth in the objection to the specification.**

d. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The additional caselaw and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed.

ii. The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K.

iii. Construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent presently claimed.

(1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the **scope** presently claimed. The claims include formulae which are much broader than the RE-TM-O formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

(a) The present specification actually shows that known forms of "a transition metal oxide", "a composition", and "a copper-oxide compound" do **not** show the onset of superconductivity at above 26°K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K." Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, non-conducting CuO phase" at p. 14, line 18.

(b) Accordingly, the present disclosure is not deemed to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88, or the "copper-oxide compound" of claim 96.

(3) The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed.

(a) With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-O", per p. 8, line 11) shows "no superconductivity".

(b) With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that **all** of the claims in this application require the critical temperature ( $T_c$ ) to be "in excess of 26°K" or "greater than 26°K".

(c) Consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims. Independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable. Those claims cannot be deemed to be fully enabled.

iv. The applicants also have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^\circ\text{K}$ . Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition

which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ...without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art." All three affiants apparently are the employees of the assignee of the present application.

(1) Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.<sup>7</sup>

(2) Those affidavits do not overcome the non-enablement rejection. The present specification discloses *on its face* that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at > 26°K.

(3) Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made. One may know *now* of a material that superconducts at more than 26°K, but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

(4) It is fully understood that the applicants are the pioneers in high temperature metal oxide superconductivity. The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims.

e. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants quote a statement from part of the previous Office Action and asserts that the "Examiner does not support this statement with any case law citations."

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<sup>7</sup>See In re Lindner, 173 USPQ 356, 358 (CCPA 1972).



(1) That assertion is incorrect. Seven decisions have been cited as providing the legal basis for this determination of non-enablement.<sup>8</sup>

(2) The applicants further "note that the Examiner seemed to have specifically avoided applying (sic) the case law and, consequently, ... applicants take the Examiner's silence as concurrence in the manner that applicants have applied this case law." Apparently, the applicants are referring to their discussion<sup>9</sup> of the caselaw previously cited by this Examiner. Notwithstanding the applicants' commentary on caselaw, the April 15, 1997 Office Action, paper no. 54, sets forth the factual basis for the determination of non-enablement at pp. 5-10.

(3) The applicants still further argues "that the Examiner does not rebut the case law and argument provided by applicants on (pages) 15-25 of their September 29, 1995 amendment which addresses (these issues) in detail." The point remains, nevertheless, that there appears to be a concurrence as to the applicable caselaw. That caselaw speaks for itself. What has been fully addressed in the previous Office Action and repeated above is the factual basis for the determination of non-enablement for the scope of the present invention.

ii. The applicants urge that "their disclosure supports a substantially broader scope than (particular) species." With respect to transition metals, the applicants point to the support in their disclosure and argue that they were enabled for transition metals other than just copper. Again, however, it is noted that high temperature superconductivity is a highly unpredictable art. In view of the record as a whole, it is again determined that one skilled in the art would not have been enabled to practice the presently disclosed invention with transition metals other than copper.

iii. The applicants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a

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<sup>8</sup>See footnotes 1-4 in the April 15, 1996 Office Action, paper no. 54. See also, the corresponding sections of this Office Action.

<sup>9</sup>See pp. 12-25 of the September 29, 1995 Amendment, paper no. 50.

whole. If the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made.

iv. The applicants assert that “(b)y the Examiner’s statement that these (statements in the affidavits) are conclusionary (sic) the Examiner appears to be placing himself up as an expert in the field of superconductivity” and “respectfully request that the Examiner submit an affidavit in the present application rebutting the position taken by applicants’ 3 affiants.” Notwithstanding those assertions, this Examiner has determined that those affidavits were insufficient because they were conclusory only, i.e., they lacked particular facts to support the conclusions reached.

v. The applicants argue that the “Examiner has provided no substantial evidence to support this assertion (of non-enabling scope of the invention). It is respectfully requested that the Examiner support (his) assertion with factual evidence and not unsupported statements.” Nevertheless, the determination of non-enabling scope is maintained for the reasons of record.

f. Applicants’ arguments filed May 1, 1998 (#64) and May 14, 1998 (#62) have been fully considered but not found to be persuasive.

i. The applicants argue that the “standard of enablement for a method of use is not the same as the standard of enablement for a composition of matter” and that their claimed invention is enabling because it is directed to a method of use rather than a composition. Basis is not seen for that argument, to the extent that it is understood. It is noted that 35 USC 112, first paragraph, reads as follows:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Process of use claims also would be subject to the statutory provisions of 35 USC 112, first paragraph.

ii. The applicants assert that the "Examiner has not shown by evidence not contained within applicants' teaching that the art of high  $T_C$  superconductors is unpredictable in view of applicants' teaching" (spelling and punctuation errors corrected). To the extent that the same assertion is understood, the rejection is maintained for the reasons of record.

iii. The applicants point to "Copper Oxide Superconductors" by Charles P. Poole, Jr., et al., (hereinafter, "the Poole article") as supporting their position that higher temperature superconductors were not that difficult to make after their original discovery.

(1) Initially, however, it should be noted that the Poole article was published *after* the priority date presently claimed. As such, it does not provide evidence of the state of the art *at the time* the presently claimed invention was made.

(2) Moreover, the present claims are directed to processes of using metal oxide superconductors, **not** processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting conditions.

(3) Finally, the Preface states in part at A3: "The unprecedented worldwide effort in superconductivity reseach that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO, and YBaCuO has emerged. ... The field of high-temperature superconductivity is still evolving ..." That preface is deemed to show that the field of high-temperature superconductivity continued to grow, on the basis of on-going basic reseach, *after* the Bednorz and Meuller article was published.

iv. The applicants submitted three affidavits, one each from Drs. Tsuei, Dinger, and Mitzi which were signed in May of 1998.

(1) Except for one change, those three affidavits are the same as the ones submitted before and discussed above.

(2) Those affidavits have been changed to indicate that the present application "includes all known principles of ceramic fabrication known at the time the application was filed." However, that additional indication also is considered to be a conclusory statement unsupported by particular evidence.

v. This Office Action is deemed to be a complete discussion of all relevant issues raised by the applicants.

**6. Claims 134, 135, and 137-142 are rejected under 35 U.S.C. 112, *first* paragraph, as based on a disclosure which is not enabling.**

a. Each of claims 134, 135, and 137-142 provide for a superconductor "having a  $T_c$  greater than 26°K", but those claims do not provide for a step of -- maintaining said (superconductor) at a temperature less than said  $T_c$  --.

b. Those claims are not enabled because they lack the critical step of maintaining the appropriate temperature for superconductivity.<sup>10</sup>

**7. Claims 86-87, 96-108, 115, 118, 120, 122, 123, 129-135, and 137-142 are rejected under 35 U.S.C. § 112, *second* paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.**

a. With respect to claims 86-87 and 96-108, the terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing.

i. The question arises: What is meant by these terms?

ii. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

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<sup>10</sup>See In re Mayhew, 527 F.2d 1229, 188 USPQ 356 (CCPA 1976).

(1) The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite.<sup>11</sup> It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

(2) The applicants respond that "(a) person of skill in the art would understand (rare earth-like) to mean that a location occupied by a rare earth element can also be occupied by another element which would have chemical properties similar enough to the rare earth elements such that it would fit in to the latter (sic - lattice?) site occupied by the rare earth element." That response does not alleviate the problem, however. Other elements may "fit" into the lattice but they may not necessarily be "rare-earth-like". It is suggested that the same language be changed to -- Group III B --, per p. 7, line 11, of the present specification.

b. Claims 112, 113, 115, 117, 118, 120, 122, and 123 are found to be indefinite for the reasons that follow.

i. In claim 112, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

ii. In claim 113, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

iii. Claim 115, lines 2-4, is indefinite with the language "forming a composition including copper, oxygen and **any** element selected from the group consisting of at least one Group IIA element and an element selected from the group consisting of a rare earth element and a Group IIIB element" (emphasis added). That language is unclear as to whether the Group IIA element must be present along with either the rare earth or Group IIIB element. It is suggested that "any" be changed to -- an -- in line 2.

iv. In claim 117, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

---

<sup>11</sup>See Ex parte Remark, 15 USPQ 2d 1498, 1500 (BPAI 1990); Ex parte Kristensen, 10 USPQ 2d 1701, 1703 (BPAI 1989); Ex parte Attig, 7 USPQ 2d 1092, 1093 (BPAI 1988); and Ex parte Copenhaver, 109 USPQ 118 (POBA 1955).

v. In claim 118, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

vi. Claim 120 is unclear the "copper oxide" of line 5 is the "transition metal" and "oxygen" of line 2.

vii. Claim 120, lines 2-4, is indefinite with the language "**any** element selected from the group consisting of at least one Group IIA element and an element selected from the group consisting of a rare earth element and a Group IIIB element" (emphasis added). That language is unclear as to whether the Group IIA element must be present along with either the rare earth or Group IIIB element. It is suggested that "any" be changed to -- an -- in line 2.

viii. In claim 122, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

ix. In claim 123, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

x. Claim 123, line 12, has the typographical error of "T T<sub>c</sub>".

c. Claims 129-142 are found to be indefinite for the reasons that follow.

i. Claim 129, last two lines, have the phrase "through said composition while exhibiting said superconductivity", which is unclear as to *what* is exhibiting superconductivity. It is suggested that the same phrase be changed to -- through said composition with said phase exhibiting said superconductivity --.

ii. Claim 130, line 3, is unclear with the term "being". It is suggested that the same term be deleted.

iii. Claim 131, line 2, apparently should have -- maintaining -- instead of "maintaing".

iv. Claim 131, line 4, is unclear with the term "therein". It is suggested that the same term be replaced with -- in said superconducting copper oxide --.

v. Claim 132, line 4, is unclear with the term "superconduting"

vi. Claim 133, line 2, has an apparent misspelling of -- maintianing --.

vii. Claim 133, line 4, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

viii. Claim 134, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

ix. Claim 135, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

x. Claim 137, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

xi. Claim 138, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

xii. Claim 139, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

xiii. Claim 140, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

xiv. Claim 141, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

xv. Claim 142, line 1, is unclear with the language "superconducting current".  
It is suggested that the same language be changed to -- superconducting electrical current --.

xvi. Claim 142, line 2, apparently should have --  $T_c$  --.

d. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants assert "that the Examiner has not responded to applicants' comments which supports applicants' position that a person of skill in the art would understand the terms 'layer-type' and 'perovskite-like' and has just repeated their rejection of the prior Office Action." That assertion is not correct, since April 15, 1996 Office Action, paper no. 54, addressed the applicants' comments at pp. 8 and 9.

ii. The prior Office Action included a proposed amendment to overcome this rejection, which has been repeated above.

e. Applicants' arguments filed May 1, 1998 (#64) and May 14, 1998 (#62) have been fully considered but not found to be persuasive. The applicants' arguments have been fully discussed above.

*Claim Rejections - 35 USC § 102*

8. Claims 24-26, 86-90, 96-135, and 137-142 are rejected under 35 U.S.C. § 102(a) as being anticipated by Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article").

a. As discussed in paper no. 20 of the ancestral application, 07/053,307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later than around December 13, 1986, the date samples were tested in the US to show superconductivity. See MPEP 715 et seq. The Asahi Shinbum article was published on November 28, 1986.

b. The reference confirms superconductivity in an oxide compound of La and Cu with Ba having a structure of the so-called perovskite structure. Although the reference fails to teach use of the testing of zero resistance for confirming superconductivity, it inherently must have been used because it is one of two methods used for testing for superconductivity (the other being diamagnetism). Accordingly, the burden of proof is upon the applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference.<sup>12</sup>

c. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The applicants argue that the Sung II Park Affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before

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<sup>12</sup>See In re Brown, 173 USPQ 685, 688; In re Best, 195 USPQ 430; and In re Marosi, 218 USPQ 289, 293.



November 9, 1986, to the best of the affiant's recollection, or no later than November 15, 1986.

The documentary evidence is not deemed to support that argument, however. See MPEP 715.07.

(1) Plots of those measurements are missing. See the Chang C. Tsuei Affidavit of March 30, 1988, para. 6. A hand-drawn diagram with the indication of vacuum pumping on November 9, 1988 also is not deemed to show that the measurements were taken.

(2) Moreover, the other evidence in the record appears to show that high temperature superconductivity was not attained in this country as of November 9 or 15, 1986. The March 30, 1986 Declaration of Richard L. Greene includes a series of cablegrams sent by Dr. Greene to the applicants in Zurich, Switzerland as Exhibit B. On both November 11, 1986 and November 14, 1986, Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperatures of 4-35°K. Exhibit C has pages dated December 1, 1986 on, and Exhibit D, which actually has plots of resistance vs. temperature, has an earliest date of December 3, 1986.

ii. The applicants assert that the Asahi Shinbum article reports a third party's confirmation of their original discovery. That assertion appears to be correct, but the article still is deemed to be prior art under 35 USC 102(a).

(1) It should be noted again, however, that the applicants' discovery was not originally made in this country and that they cannot show an earlier date than December 1986 for their invention in this country. The Asahi Shinbum article was published on November 28, 1986.

(2) The applicants cite four decisions<sup>13</sup> which do not directly apply to the present facts.

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<sup>13</sup>One decision is cited in the January 4, 1996 Supplementary Response, paper no. 51: In re Katz, 215 USPQ 14 (CCPA 1982). Three decisions are cited in the April 11, 1996 Supplementary Response, paper no. 53: Andrews v. Hovey, 123 US 267 (1887); Ex parte Lemieux, 115 USPQ 148 (POBA 1957); and Ex parte Powell and Davies, 37 USPQ 285 (POBA 1938).

(a) The In re Katz<sup>14</sup> decision held that an applicant may overcome an article as 35 USC 102(a) prior art by showing that the applicant was a co-author and that the other co-authors were under the direction and control of the applicant. Here, however, the applicants were neither co-authors in the Asahi Shinbum article nor did they exercise direction and control over the work reported in that article.

(b) The Andrews v. Hovey<sup>15</sup> decision involved a grace period which is now codified in 35 USC 102(b). The present case involves a printed publication as prior art under 35 USC 102(a).

(c) The Ex parte Powell and Davies<sup>16</sup> decision held that an applicant's own foreign patent which issued within the grace period cannot be used against him or her, and the Ex parte Lemieux<sup>17</sup> decision applied that reasoning to an applicant's own article published in another country. Again, the present applicants had no part in the writing of the Asahi Shinbum article.

(3) The present facts may raise a novel issue of law.<sup>18</sup> The applicants were the first to develop the presently claimed invention, but the earliest date they can show for

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<sup>14</sup>See In re Katz, *supra*, 215 USPQ at 17, 18. See also, MPEP 716.10.

<sup>15</sup>See Andrews v. Hovey, *supra*.

<sup>16</sup>See Ex parte Powell and Davies, *supra*, 37 USPQ at 285, 286.

<sup>17</sup>See Ex parte Lemieux, *supra*, 115 USPQ at 149. See also, MPEP 715.01(c).

<sup>18</sup>The applicants did not cite In re Mathews, 161 USPQ 276, 277-279 (CCPA 1969), which held that an applicant may overcome a patent as prior art under 35 USC 102(e) with evidence that the applicant provided the knowledge for the disclosure in that patent. By contrast, the present facts involve prior art under 35 USC 102(a) with a publication date **before** the invention was in this country.

that invention in this country is December of 1986.<sup>19</sup> The Asahi Shinbum article was published in November of 1986 and describes the development of superconductivity with an oxide of La, Ba, and Cu having a perovskite structure by a third party, but that article apparently indicates that the third party was confirming the discovery of the present applicants. Notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article still is deemed to be prior art under 35 USC 102(a), which the applicants have not been able to overcome with a showing of an earlier date in this country or a showing of their direction and control over the work done by that third party.

d. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants argue that "Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting (the inventors) on or about October 16, 1986. When these samples came into the United States since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date." As stated before repeated above, however, the applicants were unable to show the attainment of superconductivity any earlier than December 3, 1986 in this country. Again, the present invention is directed to the method of superconducting electricity. That *method* apparently was not reduced to practice before December 3, 1986.

ii. The applicants further urge that they have shown clear diligence from before November 28, 1986 until actual reduction at or around December 3, 1986. Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference.

iii. The applicants assert that they should be entitled to a one-year grace period for their own published invention, but this prior art rejection is based on 35 USC 102(a) because the author of that reference is a different inventive entity.

---

<sup>19</sup>The applicants' proposed priority date for the EPO application is January 23, 1987, which is after the December 1986 dates show by the Richard L. Greene Affidavit.

iv. The applicants argue: "If one would follow the rationale of the Examiner, if an applicant publishes an article and some other third party reports that same result prior to applicant's filing of a patent application which is subsequently filed within one year of applicant's own publication (, the) reporting of applicant's work by the third party would be prior art against applicant's application. Such a result would deny (the applicant) the one year grace period provided under 35 USC 102(b)." The applicants' argument is duly noted, but again, it is further noted that the reference is prior art under 35 USC 102(a). The reference is not just a republication of the applicants' article. Instead, the reference is the reporting of someone else's work which confirms the applicants' work. The applicants also are not able to show a priority date which pre-dates the publication of that reference. Usually, an applicant can establish an earlier priority date with an earlier foreign filing, but the EPO priority document in this case was filed on January 23, 1987, or by earlier conception and diligent reduction to practice, but in this case the invention was made outside of this country.

v. This Office Action is deemed to be a complete discussion of all relevant issues raised by the applicants.

e. Applicants' arguments filed May 1, 1998 (#64) and May 14, 1998 (#62) have been fully considered but not found to be persuasive. The applicants argue that the presently claimed invention is novel and non-obvious over the *prior* art, but for the reasons of record, however, the aforementioned reference is found to constitute prior art. The applicants' arguments have been fully discussed above.

#### ***Claim Rejections - 35 USC § 103***

9. **Claims 24-26, 86-90, 96-135, and 137-142 are rejected under 35 U.S.C. § 103 as being unpatentable over the Asahi Shinbum article.**

a. The reference is relied upon as set forth in the previous rejection. This reference may differ from the present claims in that it may fail to disclose the presently claimed method of "causing an electric current to flow in the superconductor element". It was notoriously well-known in the art of superconductors that a method of utilizing superconductive materials was to cause an electric current to flow in the material while it is cooled below its transition temperature.

See MPEP 706.02(a). Accordingly, it would have been well within the purview of one of ordinary skill to use the present claimed method with the materials disclosed by the reference. One would have been motivated to cool the material of the reference to below the transition temperature and cause electric current to flow in the material to provide electricity without resistance. Accordingly, the present claims are unpatentable in view of the prior art of record.

b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The Asahi Shinbum article is deemed to be prior art under 35 USC 102(a) for the reasons discussed above.

c. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but not found to be persuasive. The applicants' arguments have been fully discussed above.

d. Applicants' arguments filed May 1, 1998 (#64) and May 14, 1998 (#62) have been fully considered but not found to be persuasive. The applicants' arguments have been fully discussed above.

***Allowable Subject Matter***

10. Claim 136 is allowable.

11. The following is an Examiner's statement of reasons for the indication of allowable subject matter:

a. The Asahi Shinbum article teaches in general that perovskite-like compounds of La, Cu, and Ba have a  $T_c$  of 30°K, but that article apparently does not teach the particular formula in the amendment suggested above. The examples in the present specification are deemed to show criticality for that formula as recited in claim 136.

b. Support for the proposed amendment is found at p. 20, line 1, through p. 25, line 5, and in Figure 3.

c. This indication of allowable subject matter is subject to further consideration and review.

### *Conclusion*

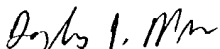
12. All claims are drawn to the same invention claimed in the application prior to the entry of the submission under 37 CFR 1.129(a) and could have been finally rejected on the grounds and art of record in the next Office action if they had been entered in the application prior to entry under 37 CFR 1.129(a).

a. Accordingly, **THIS ACTION IS MADE FINAL** even though it is a first action after the submission under 37 CFR 1.129(a). See MPEP § 706.07(b). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

b. A shortened statutory period for reply to this final action is set to expire **THREE MONTHS** from the mailing date of this action. In the event a first reply is filed within **TWO MONTHS** of the mailing date of this final action and the advisory action is not mailed until after the end of the **THREE-MONTH** shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than **SIX MONTHS** from the mailing date of this final action.

13. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Douglas J. McGinty, whose telephone number is (703) 308-3805. The examiner normally can be reached on Monday through Friday from 8:30 A.M. to 5:00 P.M., Eastern time. If *reasonable* attempts to reach the examiner by telephone are unsuccessful, however, the examiner's supervisor, Mr. Paul Lieberman, can be reached at (703) 308-2523. Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661. The fax number for this Group is (703) 305-3600.

June 24, 1998  
303561.5

  
**Douglas J. McGinty**  
**Primary Examiner**  
**Group 1100**

**IBM Corporation**

Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, NY 10598  
FAX: T/L 862-3281  
or (914) 945-3281

BY

## FACSIMILE

DATE: 5/14/98 NO. OF PAGES TO FOLLOW: 21

TO:

NAME: Examiner D. McHenry

ADDRESS: USPTO- Group 1105

PHONE NO. 703-308-3805

FAX NO. 703-305-3600 (305-3599)

FROM:

NAME: Daniel P. Morris

PHONE NO. 914-945-3217

LOCATION: IBM - Yorktown

CONTACT #: 914-945-3243

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\*\* TX STATUS REPORT \*\*

AS OF MAY 14 '98 15:00 PAGE.01

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**IN THE UNITED STATES PATENTS AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: May 14, 1998

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: June 7, 1995

Examiner: D. McGinty

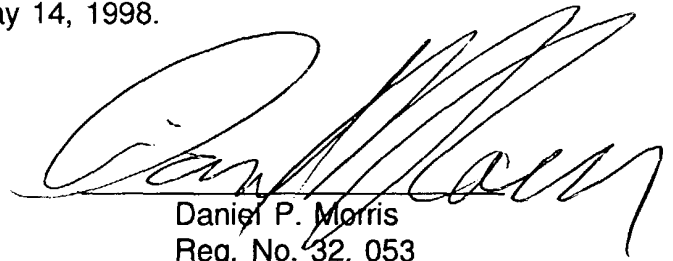
For: NEW SUPERCONDUCTOR COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATION OF TRANSMISSION**

**PURSUANT TO 37 CFR 1.8**

I hereby certify that this paper is being facsimile transmitted under Rule CFR 1.6(d)  
to the U.S. Patent and Trademark Office on May 14, 1998.



Daniel P. Morris  
Reg. No. 32, 053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, NY 10598  
(914) 945-3217

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**SUPPLEMENTARY AMENDMENT**

Sir:

In response to the Office Action dated September 27, 1997 please consider the  
following:

Enclosed herewith are affidavits of J. Bednorz, Timothy  
Dinger and David B. Mitzi. These affidavits were submitted earlier by  
the same applicants with the characterization of the invention includes all  
known principles of ceramic superconductivity. This characterization was filed.

**REMARKS**

In the prosecution of this application applicants have referred to the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1988). This book shall be referred to herein as Poole et al.. The preface of this book says "[t]his volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 123 K, from the time of its discovery by Bednorz and Muller in April 1986 until a few months after the award of the Nobel Prize to them in October, 1987. " This passage is referring to applicants and their paper referred to at page 6 of applicants' specification. This book acknowledges that applicants are the discoverers of the field of high temperature superconductivity. (See Attachment A)

Applicants note that it is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by applicants that transition metal oxides are high  $T_c$  superconductors. Chapter 5 of the Poole et al. book entitled Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. " Poole et al. further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors,

and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole et al. further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La Sr, Tl, Y, or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20 hr) at elevated temperatures (~900°C ). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by applicants and as generally described at pages 8, line 19, to page 9, line 5, of applicants' specification which states "The methods by which these superconductive compositions can be made can use known principles of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal." ( See Attachment A)

Consequently, applicants have fully enabled high TC transition metal oxides and their claims.

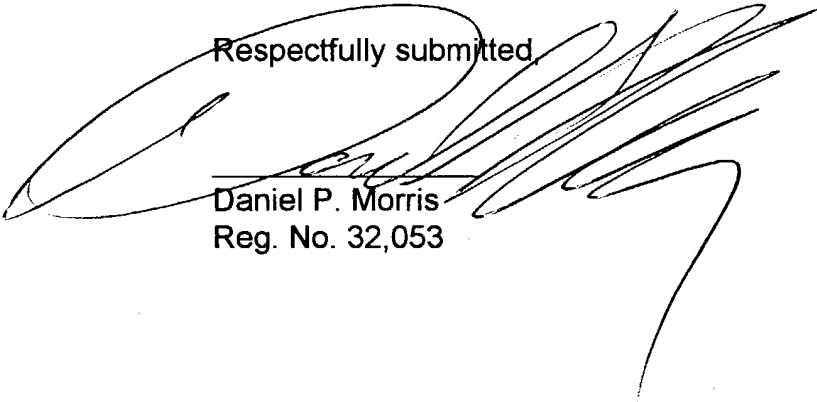
In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner

wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

  
Daniel P. Morris  
Reg. No. 32,053

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598  
(914) 945-3216

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

: Date: May 14, 1998

Serial No.: 08/303,561

: Group Art Unit: 1105

Filed: September 9, 1994

: Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Chang C. Tsuei, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Mechanical Engineering from National Taiwan University (1960) and M. S. and PhD. degrees, in Material Science (1963, 1966) respectively from California Institute of Technology.

That I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1973 to the present. (See attached Exhibit A for other professional employment history.)

That I have worked in the fabrication of and characterization of superconductors and related materials from 1973 to the present.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of  
YO987-074BY

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

By: Chang C. Tsuei  
Chang C. Tsuei

Sworn to before me this 12<sup>th</sup> day of May, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
In Westchester County  
Commission Expires July 5, 1998

CHANG C. TSUEI

Education

California Institute of Technology, M.S. (1963), Ph.D. (1966)

National Taiwan University, B.S. (1960)

Professional Employment

1993 - present - Research Staff Member

1983 - 1993 - Manager, Physics of Structured Materials

1979 - 1983 - Manager, Physics of Amorphous Materials

1974 - 1975 - Acting Manager, Superconductivity

1973 - 1979 - Research Staff Member

Harvard University: 1980 (Summer)

Visiting Scholar in Applied Physics

Stanford University: 1982 (Sept.) - 1983 (April)

Visiting Scholar in Applied Physics

California Institute of Technology

1972 - 1973 - Senior Research Associate in Applied Physics

1969 - 1972 - Senior Research Fellow in Materials Science

1966 - 1969 - Research Fellow in Materials Science

Exhibit A

YO987-074BY



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

: Date: May 14, 1998

Serial No.: 08/303,561

: Group Art Unit: 1105

Filed: September 9, 1994

: Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Timothy Dinger, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M. S. degree (1983) and a PhD. degree (1986), both in Material Science from the University of California at Berkley.

That I have worked as a research staff member in Material Science at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1986 to the present.

That I have worked in the fabrication of and characterization of superconductors and related materials from 1987 to 1991.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of

YO987-074BY

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar way, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

By: Timothy R. Dinger  
Timothy Dinger

Sworn to before me this 6<sup>th</sup> day of May, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
In Westchester County  
Commission Expires July 5, 1998

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

J. Bednorz et al.

: Date: May 14, 1998

Serial No.: 08/303,561

: Group Art Unit: 1105

Filed: September 9, 1994

: Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, David B. Mitzi, being duly sworn, do hereby depose and state:

That I received a B. S. E. degree in Electrical Engineering/Engineering Physics (1985) from Princeton University and a PhD. degree, in Applied Physics (1990) from Stanford University, California.

That I have worked as a research staff member in Solid State Chemistry at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1990 to the present.

That I have worked in the fabrication of and characterization of superconductors and related materials from 1990 to the present.

That I have reviewed the above-identified patent application and that I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and

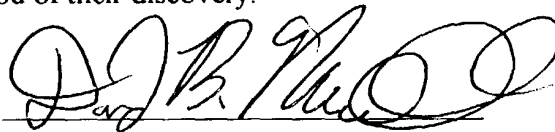
YO987-074BY

Muller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

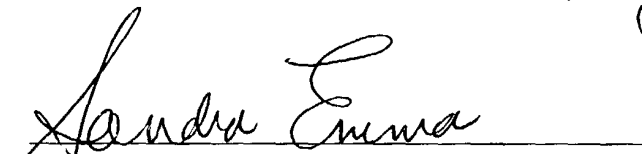
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By:



David B. Mitzi

Sworn to before me this 6<sup>th</sup> day of May, 1998



Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
In Westchester County  
Commission Expires July 5, 1998 *98*

**ATTACHMENT A**

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# **COPPER OXIDE SUPERCONDUCTORS**

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**Charles P. Poole, Jr.**  
**Timir Datta**  
**Horacio A. Farach**

*with help from*

**M. M. Rigney**  
**C. R. Sanders**

*Department of Physics and Astronomy  
University of South Carolina  
Columbia, South Carolina*



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p. cm.

"A Wiley-Interscience publication."

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## PREFACE

The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. The time is now ripe to bring together in one place the results of this research effort so that scientists working in this field can better acquire an overall perspective, and at the same time have available in one place a collection of detailed experimental data. This volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 120 K, from the time of its discovery by Bednorz and Müller in April 1986 until a few months after the award of the Nobel Prize to them in October 1987. During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as  $\text{BiSrCaCuO}$ ,  $\text{LaSrCuO}$ ,  $\text{TlBaCaCuO}$ , and  $\text{YBa-CuO}$  has emerged. At the same time there has been a continual debate on the extent to which the BCS theory and the electron-phonon interaction mechanism apply to the new materials, and new theoretical models are periodically proposed. We discuss these matters and, when appropriate, make comparisons with transition metal and other previously known superconductors. Many of the experimental results are summarized in figures and tables.

The field of high-temperature superconductivity is still evolving, and some ideas and explanations may be changed by the time these notes appear in print. Nevertheless, it is helpful to discuss them here to give insights into work now in progress, to give coherence to the present work, and to provide guidance for future work. It is hoped that in the not too distant future the field will settle down enough to permit a more definitive monograph to be written.



vi PREFACE

The literature has been covered almost to the end of 1987, and some 1988 work has been discussed. This has been an enormous task, and we apologize for any omissions in the citing and discussion of articles.

We wish to thank the following for giving us some advanced notice about their work: R. Barrio, B. Battlogg, L. A. Boatener, G. Burns, J. Drumheller, H. Enomoto, P. K. Gallagher, R. Goldfarb, J. E. Graebner, R. L. Greene, J. Heremans, T. C. Johnson, J. K. Karamas, M. Levy, J. W. Lynn, A. Malozemoff, K. A. Müller, T. Nishino, N. Nucker, J. C. Phillips, R. M. Silver, G. Shirane, J. Stankowski, B. Stridzker, S. Tanigawa, G. A. Thomas, and W. H. Weber. We appreciate comments on the manuscript from S. Alterowitz, C. L. Chien, D. K. Finnamore, J. Goodenough, J. R. Morton, and C. Uher, and helpful discussions with J. Budnick, M. H. Cohen, M. L. Cohen, R. Creswick, S. Deb, M. Fluss, A. Freeman, D. U. Gubser, A. M. Hermann, V. Z. Kresin, H. Ledbetter, W. E. Pickett, M. Tinkham, C. E. Violet, and S. A. Wolf. Support from the University of South Carolina, the Naval Research Laboratory, and the National Science Foundation Grant ISP 80 11451 is gratefully acknowledged.

Michael A. Poole helped to develop the computer data storage techniques that were used. Jesse S. Cook is thanked for editorial comments on the manuscript. C. Almasan, S. Atkas, J. Estrada, N. Hong, O. Lopez, M. Mesa, T. Mouzghi, and T. Usher are thanked for their interest in this project.

CHARLES P. POOLE, JR.  
TIMIR DATTA  
HORACIO A. FARACH

*Columbia, South Carolina  
July 1988*

ects of the BCS theory, however,  
id detailed treatment of the prop-  
see the extent to which they con-  
ey agree with some of the other  
n these two chapters.

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# V

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## PREPARATION AND CHARACTERIZATION OF SAMPLES

### A. INTRODUCTION

Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. Nevertheless, it should be emphasized that the preparation of these samples does involve some risks since the procedures are carried out at quite high temperatures, often in oxygen atmospheres. In addition, some of the chemicals are toxic, and in the case of thallium compounds the degree of toxicity is extremely high so ingestion, inhalation, and contact with the skin must be prevented.

The superconducting properties of the copper oxide compounds are quite sensitive to the method of preparation and annealing. Multiphase samples containing fractions with  $T_c$  above liquid nitrogen temperature (Monec) can be synthesized using rather crude techniques, but really high-grade single-phase specimens require careful attention to such factors as temperature control, oxygen content of the surrounding gas, annealing cycles, grain sizes, and pelletizing procedures. The ratio of cations in the final sample is important, but even more critical and more difficult to control is the oxygen content. However, in the case of the Bi- and Tl-based compounds, the superconducting properties are less sensitive to the oxygen content.

Figure V-1 illustrates how preparation conditions can influence superconducting properties. It shows how the calcination temperature, the annealing time, and the quenching conditions affect the resistivity drop at  $T_c$  of a BiSrCa-CuO pellet, a related copper-enriched specimen, and an aluminum-doped coun-

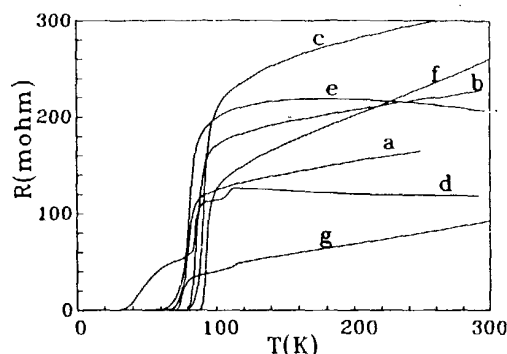


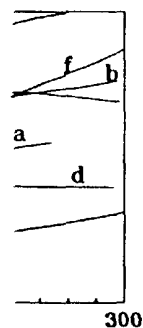
Fig. V-1. Effects of heat treatments on the resistivity transition of  $\text{BiSrCaCuO}_{7-x}$  (a) calcined at  $860^\circ\text{C}$ , (b) calcined at  $885^\circ\text{C}$ , (c) calcined at  $901^\circ\text{C}$ , (d) aluminum-doped sample calcined at  $875^\circ\text{C}$ , prolonged annealing, (e) copper-rich sample calcined at  $860^\circ\text{C}$ , (f) aluminum-doped sample calcined at  $885^\circ\text{C}$ , slow quenching and (g) calcined at  $885^\circ\text{C}$ , prolonged annealing, and slow quenching (Chuz5).

terpart (Chuz5). These samples were all calcined and annealed in the same temperature range and air-quenched to room temperature.

Polycrystalline samples are the easiest to prepare, and much of the early work was carried out with them. Of greater significance is work carried out with thin films and single crystals, and these require more specialized preparation techniques. More and more of the recent work has been done with such samples.

Many authors have provided sample preparation information, and others have detailed heat treatments and oxygen control. Some representative techniques will be discussed.

The beginning of this chapter will treat methods of preparing bulk superconducting samples in general, and then samples of special types such as thin films and single crystals. The remainder of the chapter will discuss ways of checking the composition and quality of the samples. The thermodynamic or subsolidus phase diagram of the ternary Y-Ba-Cu oxide system illustrated in Fig. V-2 contains several stable stoichiometric compounds such as the end-point oxides  $\text{Y}_2\text{O}_3$ , BaO, and CuO at the apices, the binary oxides stable at  $950^\circ$ ,  $(\text{Ba}_2\text{CuO}_4)$ ,  $\text{Ba}_2\text{CuO}_3$ ,  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ ,  $\text{Y}_4\text{Ba}_3\text{O}_9$ ,  $\text{Y}_2\text{BaO}_4$ , and  $(\text{Y}_2\text{Ba}_4\text{O}_7)$ , along the edges, and ternary oxides such as  $(\text{YBa}_3\text{Cu}_2\text{O}_7)$ , the semiconducting green phase  $\text{Y}_2\text{BaCuO}_5$ , and the superconducting black solid  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in the interior (Beye2, Bour3, Capo1, Eag11, Frase, Hosoy, Jone1, Kaise, Kurth, Kuzz, Leez3, Lian1, Mali1, Schni, Schn1, Schu1, Takay, Torra, Wagne). Compounds in parentheses are not on the figure, but are reported by other workers. The existence of a narrow range of solid solution was reported (Panso), and then argued against (Wagne) by the same group.



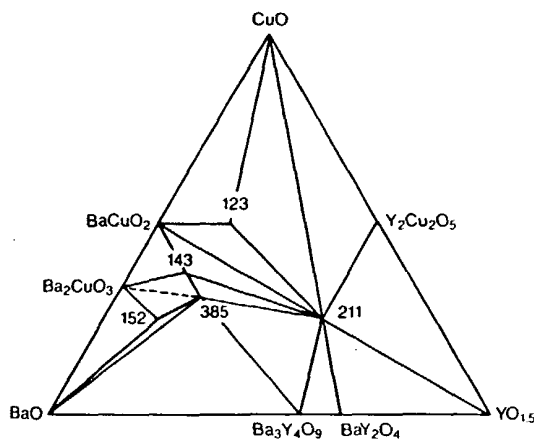
ransition of  $\text{BiSrCaCuO}_{7-\delta}$  (a) at  $901^\circ\text{C}$ , (d) aluminum-doped copper-rich sample calcined at low quenching and (g) calcined (25).

annealed in the same temperature.

and much of the early work was carried out with thin specialized preparation techniques done with such samples.

information, and others. Some representative techniques

preparing bulk superconducting types such as thin films. I discuss ways of checking thermodynamic or subsolidus illustrated in Fig. V-2 consists as the end-point oxides stable at  $950^\circ$ , ( $\text{Ba}_3\text{CuO}_4$ ), and ( $\text{Y}_2\text{Ba}_4\text{O}_7$ ), along the nonconducting green phase  $\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  in the interior (1, Kaise, Kurth, Kuzzz, Wra, Wagne). Compounds used by other workers. The sorted (Panso), and then



| Compound   | Slowly cooled to room temperature |
|--|-----------------------------------|
| 123 - $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$           | $\text{O}_7$                      |
| 143 - $\text{YBa}_4\text{Cu}_3\text{O}_{8.5+\delta}$           | $\text{O}_9$                      |
| 385 - $\text{Y}_3\text{Ba}_8\text{Cu}_5\text{O}_{17.5+\delta}$ | $\text{O}_{18}$                   |
| 152 - $\text{YBa}_5\text{Cu}_2\text{O}_{8.5+\delta}$           | $\text{O}_9$                      |
| 211 - $\text{Y}_2\text{BaCuO}_5$                               |                                   |
| $\text{Ba}_2\text{CuO}_{3+\delta}$                             | $\text{O}_{3.3}$                  |

Fig. V-2. Ternary phase diagram of the  $\text{Y}_2\text{O}_3$ - $\text{BaO}$ - $\text{CuO}$  system at  $950^\circ\text{C}$ . The green phase [ $\text{Y}_2\text{BaCuO}_5$ , (211)] the superconducting phase [ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (123)], and three other compounds are shown in the interior of the diagram (DeLee).

## B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol-gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at  $500^\circ\text{C}$  before calcination

(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period ( $\approx 20$  hr) at elevated temperatures ( $\approx 900^\circ\text{C}$ ). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajk1, Hatan, Herrm, Hikal, Hirab, Jayar, Maen1, Mood1, Mood2, Neume, Poepp, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawa1, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol-gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for YBaCuO as well (Cimaz, Hatfi).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the YBa\* material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around  $900^\circ\text{C}$  for 15 hr. During this time the YBaCuO mixture changes color from the green  $\text{Y}_2\text{BaCuO}_5$  phase to the dark gray  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-

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For: NEW SUPERCONDUCTOR COMPOUNDS HAVING HIGH TRANSITION ...  
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Received in the U.S. Patent & Trademark Office: \_\_\_\_\_  
No. of pages of specification \_\_\_\_ : No. of pages of claims \_\_\_\_  
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In re application of: J. Bednorz et al.  
For: NEW SUPERCONDUCTOR COMPOUNDS HAVING HIGH TRANSITION ...  
Serial No Q8/303,561 ; Docket No.: Y0987-074BY Atty.: DPM  
Received in the U.S. Patent & Trademark Office: \_\_\_\_\_  
No. of pages of specification \_\_\_\_ : No. of pages of claims \_\_\_\_  
No. of sheets of drawings: \_\_\_\_\_  
Declaration is attached to specification.  
All fees are charged to our Account No. 09-0468

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Date: April 27, 1998

J. Bednorz et al.

Group: 1105

Serial No.: 08/303,561

Examiner: D. McGinty

Filed: September 9, 1994

Docket No. YO987-074BY

For: NEW SUPERCONDUCTOR COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

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Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)**

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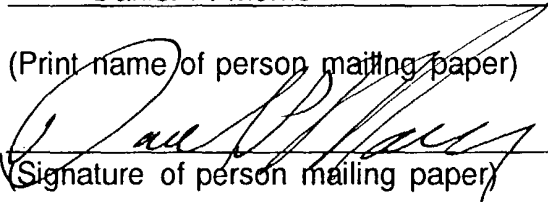
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Daniel P. Morris

(Print name of person mailing paper)

  
(Signature of person mailing paper)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: November 28, 1997

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

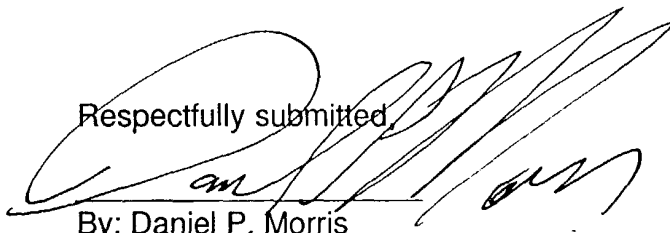
**Submission after final rejection under 37 CFR 1.129 (a)**

In response to the final rejection dated August 27, 1997 please consider the following:

The above identified applica <sup>↑ may</sup> \_\_\_\_\_ ears as of June 8,  
1995 and has been finally re \_\_\_\_\_ filed. Applicants  
request that the amendment \_\_\_\_\_ e merits under 37  
CFR 1.129 (a). This is a sec \_\_\_\_\_ h is permitted  
thereunder.

Please charge deposit account \_\_\_\_\_ enter this paper and the  
amendment attached herewith.

Respectfully submitted,

  
By: Daniel P. Morris  
Attorney



**AMENDMENT**

Sir:

In response to the Office Action dated September 27, 1997 please consider the following:

**IN THE CLAIMS**

129. (Added) A method comprising providing a composition having a transition temperature greater than 26°K, the composition including a rare earth or alkaline earth element, a transition metal element capable of exhibiting multivalent states and oxygen, including at least one phase that exhibits superconductivity at temperature in excess of 26°K, maintaining said composition at said temperature to exhibit said superconductivity and passing an electrical superconducting current through said composition while exhibiting said superconductivity.

130. (Added) A method comprising providing a superconducting transition metal oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting transition metal oxide being at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

131. (Added) A method comprising providing a superconducting copper oxide having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein.

132. (Added) A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein, said composition comprising at least one each of rare earth, an alkaline earth, and copper.

133. (Added) A method comprising providing a superconducting oxide composition having a superconductive onset temperature greater than 26°K, maintaining said superconducting copper oxide at a temperature less than said superconducting onset temperature and flowing a superconducting current therein, said composition comprising at least one each of a group IIIB element, an alkaline earth, and copper.

134. (Added) A method comprising flowing a superconducting current in a transition metal oxide having a  $T_c$  greater than 26°K.

135. (Added) A method comprising flowing a superconducting current in a copper oxide having a  $T_c$  greater than 26°K.

136(Added). A method comprising the steps of:

forming a composition of the formula  $Ba_xLa_{x-5}Cu_5O_y$ , wherein x is from about 0.75 to about 1 and y is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical current through said composition while said metal oxide phase is in said superconducting state.

137. (Added) A method comprising flowing a superconducting current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a IIIB element, an alkaline earth, and copper oxide.

138. (Added) A method comprising flowing a superconducting current in a composition of matter having a  $T_c$  greater than 26°K, said composition comprising at least one each of a rare earth, an alkaline earth, and copper oxide.

139. (Added) A method comprising flowing a superconducting current in a composition of matter having a  $T_c$  greater than  $26^\circ\text{K}$ , said composition comprising at least one each of a rare earth, and copper oxide.

140. (Added) A method comprising flowing a superconducting current in a composition of matter having a  $T_c$  greater than  $26^\circ\text{K}$  carrying, said composition comprising at least one each of a IIIB element, and copper oxide.

141. (Added) A method comprising flowing a superconducting current in a transition metal oxide comprising a  $T_c > 26^\circ\text{K}$ .

142. (Added) A method comprising flowing a superconducting current in a copper oxide comprising a  $T_c > 26^\circ\text{K}$ .

## REMARKS

Claim 129 - 142 are added.

### Claim Rejections - 35 USC § 112

The specification has been objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

Applicants respectfully disagree for the reasons given below.

The Examiner states that "[t]he present specification is deemed to be enabled only for compositions comprising  $Ba_xLa_{5-x}Cu_5O_y$ ." Applicants respectfully disagree. Applicants are not claiming a composition of matter or a method of forming a composition of matter. Applicants are claiming a method of flowing or passing a superconducting current through a high  $T_c$  superconducting material.

The Examiner further states that "[t]he art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties." Applicants' claims are not directed to a composition of matter. Applicants' claims are directed to an a superconducting current flowing therein or carrying a superconducting current. The superconducting component is a transition metal oxide. Applicants discovered that transition metal oxides have superconducting onset or transition temperatures greater than 26°K. Applicants have enabled what they have discovered and claimed. The

Examiner's statement that "[s]mall changes in composition can result in dramatic changes in or loss of superconducting properties." has not been supported by any evidence not contained within applicants' teaching. Any teaching by applicants about the amounts of constituent and processing steps is part of applicants' enabling disclosure.

The Examiner further states that "[t]he amount and type of examples necessary to support broad claims increases as the predictability of the art decreases." Once applicants discovered that transition metal oxides were superconducting at temperatures greater than 26°K., it was within the skill of the art to apply applicants teaching to use other specific examples of transition metal oxide compounds for the methods claimed. The Examiner has not shown by evidence not contained within applicants teaching that the art of high TC superconductors is unpredictable in view of applicants' teaching.

The Examiner further states that "[c]laims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112." The Examiner has not shown that the claims are broad enough to cover a large number of compositions that fail. Again the Examiner is applying an incorrect standard. The Examiner is applying a standard applicable to composition of matter. Applicants are not claiming a composition of matter. As shown by applicants prior comments applicants have in fact fully enabled the composition of matter. Therefore,

applicants have provided excess enablement for the claimed invention. The standard of enablement for a method of use is not the same as the standard of enablement for a composition of matter. Notwithstanding, it is well settled law that claims to a composition of matter can encompass a number of inoperable species. Applicants' claims do not cover inoperable species. The claims only encompass methods of flowing a superconducting current in transition metal oxides that are superconducting at temperatures in excess of 26°K. Those transition metal oxides that are not superconducting at temperatures in excess of 26°K are not encompassed by applicants claims reciting these limitations. Applicants note that a claim to a composition of matter is dominant to any use of that composition of matter and claims directed to a method of use of a composition of matter are necessarily of narrower scope than claims to the composition of matter. Applicants' claims do not encompass uses other than those to which the claims are limited to by the use limitations recited in the claims. Applicants' claims are directed to what they have discovered. Therefore, applicants' claims fully satisfy the requirements of 35 USC 112.

The Examiner further states that "[m]erely reciting a desired result does not overcome this failure." Applicants' claims do not "merely recite a desired result". Some claims recite flowing or passing passing a superconducting current through the material. Other claims recite "a superconducting current flowing " or "carrying a superconducting current" . This is not " a desired result", but an actual action occurring. If an apparatus, structure, device or invention is made with material that is not superconducting at temperatures in excess of 26°K , such mehtods, apparatus,

structure, device or invention will not be encompassed by the method claims reciting this limitation. Again applicants' claims are not directed to a chemical composition.

The Examiner further states "[i]n particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity?" The claims do not cover "any layered perovskite". The claims do not cover a material. The claims cover a method of using a material. Only those method, apparatuses, structures, devices or inventions using the recited methods of the claims are covered by the claims. The Examiner is again applying an incorrect standard, a standard applicable to a chemical composition which is dominant to all uses of the chemical composition. Applicants' note, however, that they have fully enabled the compositions.

The Examiner further states "[i]t should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood." Whether or not this statement is true or not true is of no relevance to applicants claims which are directed to methods using the compositions. The mechanism does not have to be understood to use the material as claimed by applicants. Applicants have discovered that transition metal oxides are useful passing or flowing superconducting currents therein at temperatures in excess of 26°K. The Examiner's comments, if applicable, are applicable to claims directed to specific chemical compounds but not to applicants claims. Nor would they be applicable to generic composition claims.



The Examiner further states "[a]ccordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity." Again this comment is not applicable to claims directed to methods of passing or flowing superconducting currents as claimed. Applicants have discovered that transition metal oxides are superconducting at temperatures in excess of 26°K are useful for methods as claimed.

The Examiner further states "[a] patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion' ". Applicants are not claiming specific compounds that they have not described. Applicants are generically and specifically claiming what they have discovered. Thus applicants are not "hunting" for anything. Applicants successful conclusion is their discovery that transition metal oxides are superconducting at temperatures in excess of 26°K and can thus be used for methods of passing superconducting currents therein as claimed.

In the discussion in the prosecution of this application applicants have frequently referred to the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1988). This book shall be referred to herein as Poole et al.. The preface of this book says "[t]his volume reviews the experimental aspects of the field of oxide superconductivity with transition

temperatures from 30 K to above 123 K, from the time of its discovery by Bednorz and Muller in April 1986 until a few months after the award of the Nobel Prize to them in October, 1987. " This passage is referring to applicants and their paper referred to at page 6 of applicants' specification. This book acknowledges that applicants are the discoverers of the field of high temperature superconductivity. (See Attachment A)

Applicants note that it is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by applicants that transition metal oxides are high  $T_c$  superconductors. Chapter 5 of the Poole et al. book entitled *Preparation and Characterization of Samples* states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. " Poole et al. further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole et al. further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. ... These compounds are mixed in the desired atomic ratios and

ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20 hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by applicants and as generally described at pages 8, line 19, to page 9, line 5, of applicants' specification which states "The methods by which these superconductive compositions can be made can use known principles of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal." ( See Attachment A)

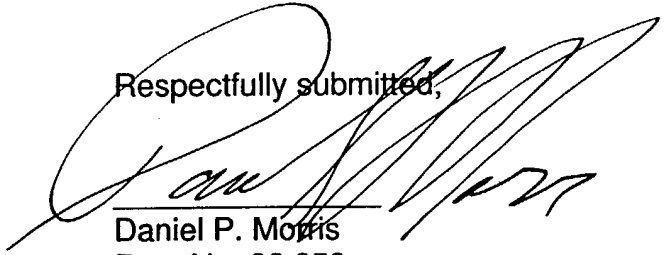
Consequently, applicants have fully enabled high  $T_c$  transition metal oxides and their claims.

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,



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**ATTACHMENT A**

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# COPPER OXIDE SUPERCONDUCTORS

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**Timir Datta**  
**Horacio A. Farach**

*with help from*

**M. M. Rigney**  
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## PREFACE

The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. The time is now ripe to bring together in one place the results of this research effort so that scientists working in this field can better acquire an overall perspective, and at the same time have available in one place a collection of detailed experimental data. This volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 120 K, from the time of its discovery by Bednorz and Müller in April 1986 until a few months after the award of the Nobel Prize to them in October 1987. During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as  $\text{BiSrCaCuO}$ ,  $\text{LaSrCuO}$ ,  $\text{TlBaCaCuO}$ , and  $\text{YBaCuO}$  has emerged. At the same time there has been a continual debate on the extent to which the BCS theory and the electron-phonon interaction mechanism apply to the new materials, and new theoretical models are periodically proposed. We discuss these matters and, when appropriate, make comparisons with transition metal and other previously known superconductors. Many of the experimental results are summarized in figures and tables.

The field of high-temperature superconductivity is still evolving, and some ideas and explanations may be changed by the time these notes appear in print. Nevertheless, it is helpful to discuss them here to give insights into work now in progress, to give coherence to the present work, and to provide guidance for future work. It is hoped that in the not too distant future the field will settle down enough to permit a more definitive monograph to be written.



vi PREFACE

The literature has been covered almost to the end of 1987, and some 1988 work has been discussed. This has been an enormous task, and we apologize for any omissions in the citing and discussion of articles.

We wish to thank the following for giving us some advanced notice about their work: R. Barrio, B. Battlogg, L. A. Boatener, G. Burns, J. Drumheller, H. Enomoto, P. K. Gallagher, R. Goldfarb, J. E. Graebner, R. L. Greene, J. Heremans, T. C. Johnson, J. K. Karamas, M. Levy, J. W. Lynn, A. Malozemoff, K. A. Müller, T. Nishino, N. Nucker, J. C. Phillips, R. M. Silver, G. Shirane, J. Stankowski, B. Stridzker, S. Tanigawa, G. A. Thomas, and W. H. Weber. We appreciate comments on the manuscript from S. Alterowitz, C. L. Chien, D. K. Finnamore, J. Goodenough, J. R. Morton, and C. Uher, and helpful discussions with J. Budnick, M. H. Cohen, M. L. Cohen, R. Creswick, S. Deb, M. Fluss, A. Freeman, D. U. Gubser, A. M. Hermann, V. Z. Kresin, H. Ledbetter, W. E. Pickett, M. Tinkham, C. E. Violet, and S. A. Wolf. Support from the University of South Carolina, the Naval Research Laboratory, and the National Science Foundation Grant ISP 80 11451 is gratefully acknowledged.

Michael A. Poole helped to develop the computer data storage techniques that were used. Jesse S. Cook is thanked for editorial comments on the manuscript. C. Almasan, S. Atkas, J. Estrada, N. Hong, O. Lopez, M. Mesa, T. Mouzghi, and T. Usher are thanked for their interest in this project.

CHARLES P. POOLE, JR.  
TIMIR DATTA  
HORACIO A. FARACH

*Columbia, South Carolina  
July 1988*

A4

ects of the BCS theory, however,

d detailed treatment of the prop-  
see the extent to which they con-  
ey agree with some of the other  
a these two chapters.

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# V

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## PREPARATION AND CHARACTERIZATION OF SAMPLES

### A. INTRODUCTION

Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. Nevertheless, it should be emphasized that the preparation of these samples does involve some risks since the procedures are carried out at quite high temperatures, often in oxygen atmospheres. In addition, some of the chemicals are toxic, and in the case of thallium compounds the degree of toxicity is extremely high so ingestion, inhalation, and contact with the skin must be prevented.

The superconducting properties of the copper oxide compounds are quite sensitive to the method of preparation and annealing. Multiphase samples containing fractions with  $T_c$  above liquid nitrogen temperature (Monec) can be synthesized using rather crude techniques, but really high-grade single-phase specimens require careful attention to such factors as temperature control, oxygen content of the surrounding gas, annealing cycles, grain sizes, and pelletizing procedures. The ratio of cations in the final sample is important, but even more critical and more difficult to control is the oxygen content. However, in the case of the Bi- and Tl-based compounds, the superconducting properties are less sensitive to the oxygen content.

Figure V-1 illustrates how preparation conditions can influence superconducting properties. It shows how the calcination temperature, the annealing time, and the quenching conditions affect the resistivity drop at  $T_c$  of a BiSrCa-CuO pellet, a related copper-enriched specimen, and an aluminum-doped coun-

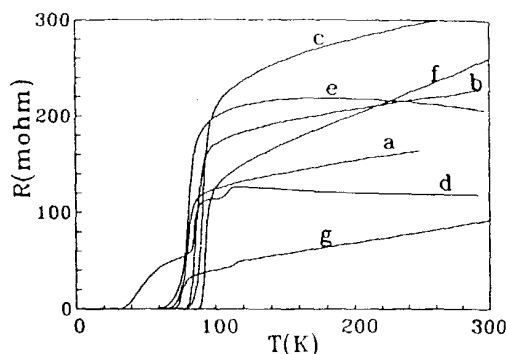


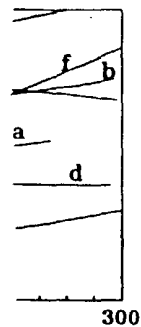
Fig. V-1. Effects of heat treatments on the resistivity transition of  $\text{BiSrCaCuO}_{7-x}$  (a) calcined at  $860^\circ\text{C}$ , (b) calcined at  $885^\circ\text{C}$ , (c) calcined at  $901^\circ\text{C}$ , (d) aluminum-doped sample calcined at  $875^\circ\text{C}$ , prolonged annealing, (e) copper-rich sample calcined at  $860^\circ\text{C}$ , (f) aluminum-doped sample calcined at  $885^\circ\text{C}$ , slow quenching and (g) calcined at  $885^\circ\text{C}$ , prolonged annealing, and slow quenching (Chuz5).

terpart (Chuz5). These samples were all calcined and annealed in the same temperature range and air-quenched to room temperature.

Polycrystalline samples are the easiest to prepare, and much of the early work was carried out with them. Of greater significance is work carried out with thin films and single crystals, and these require more specialized preparation techniques. More and more of the recent work has been done with such samples.

Many authors have provided sample preparation information, and others have detailed heat treatments and oxygen control. Some representative techniques will be discussed.

The beginning of this chapter will treat methods of preparing bulk superconducting samples in general, and then samples of special types such as thin films and single crystals. The remainder of the chapter will discuss ways of checking the composition and quality of the samples. The thermodynamic or subsolidus phase diagram of the ternary Y-Ba-Cu oxide system illustrated in Fig. V-2 contains several stable stoichiometric compounds such as the end-point oxides  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ , and  $\text{CuO}$  at the apices, the binary oxides stable at  $950^\circ$ ,  $(\text{Ba}_2\text{CuO}_4)$ ,  $\text{Ba}_2\text{CuO}_3$ ,  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ ,  $\text{Y}_4\text{Ba}_3\text{O}_9$ ,  $\text{Y}_2\text{Ba}_4\text{O}_7$ , and  $(\text{Y}_2\text{Ba}_4\text{O}_7)$ , along the edges, and ternary oxides such as  $(\text{YBa}_2\text{Cu}_3\text{O}_{7-x})$ , the semiconducting green phase  $\text{Y}_2\text{BaCuO}_5$ , and the superconducting black solid  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in the interior (Beye2, Bour3, Capo1, Eagl1, Frase, Hosoy, Jone1, Kaise, Kurth, Kuzz, Leez3, Lian1, Mali1, Schni, Schn1, Schu1, Takay, Torra, Wagne). Compounds in parentheses are not on the figure, but are reported by other workers. The existence of a narrow range of solid solution was reported (Panso), and then argued against (Wagne) by the same group.



transition of  $\text{BiSrCaCuO}_{7-\delta}$  (a) at  $901^\circ\text{C}$ , (d) aluminum-doped copper-rich sample calcined at slow quenching and (g) calcined (z5).

annealed in the same temperature.

and much of the early work was carried out with thin-film specialized preparation techniques done with such samples.

information, and others. Some representative techniques

preparing bulk superconductor types such as thin films. I discuss ways of checking thermodynamic or subsolidus data illustrated in Fig. V-2 concerning the end-point oxides stable at  $950^\circ$ , ( $\text{Ba}_3\text{CuO}_4$ ), and ( $\text{Y}_2\text{Ba}_4\text{O}_7$ ), along the nonconducting green phase  $\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  in the interior (Kaise, Kurth, Kuzzz, Werra, Wagne). Compounds reported by other workers. The reported (Panso), and then

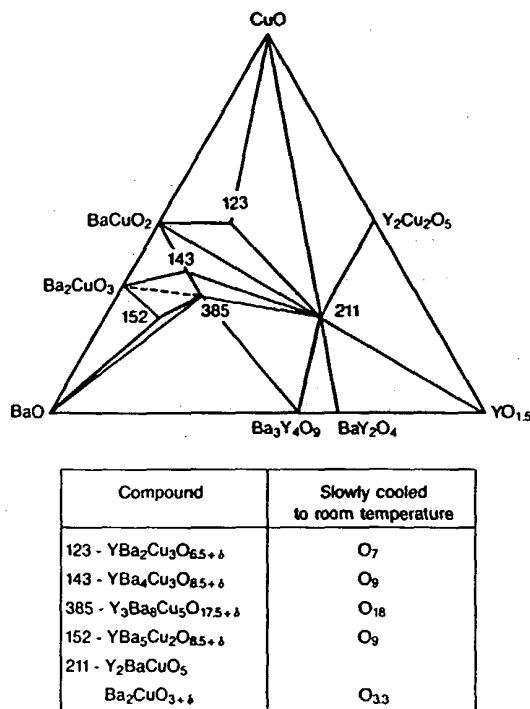


Fig. V-2. Ternary phase diagram of the  $\text{Y}_2\text{O}_3$ - $\text{BaO}$ - $\text{CuO}$  system at  $950^\circ\text{C}$ . The green phase [ $\text{Y}_2\text{BaCuO}_5$ , (211)] the superconducting phase [ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (123)], and three other compounds are shown in the interior of the diagram (DeLee).

## B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol-gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at  $500^\circ\text{C}$  before calcination

(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period ( $\approx 20$  hr) at elevated temperatures ( $\approx 900^\circ\text{C}$ ). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajk1, Hatan, Herrm, Hikal, Hirab, Jayar, Maen1, Mood1, Mood2, Neume, Poepp, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawa1, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol-gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for YBaCuO as well (Cimaz, Hatfi).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the YBa\* material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around  $900^\circ\text{C}$  for 15 hr. During this time the YBaCuO mixture changes color from the green  $\text{Y}_2\text{BaCuO}_5$  phase to the dark gray  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-

# Appendix A

EUROPEAN PATENT APPLICATION

Application number: 87100961.9

Int. Cl.<sup>4</sup> H01L 39/12

Date of filing: 23.01.87

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Designated Contracting States:  
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New superconductive compounds of the K<sub>2</sub>NiF<sub>4</sub> structural type having a high transition temperature, and method for fabricating same.

The superconductive compounds are oxides of the general formula RE<sub>2-x</sub>AE<sub>x</sub>TM.O<sub>4-y</sub>, wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two member of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ . The method for making these compounds involves the steps of coprecipitating aqueous solutions of the respective nitrates of the constituents and adding the coprecipitate to oxalic acid, decomposing the precipitate and causing a solid-state reaction at a temperature between 500 and 1200°C for between one and eight hours, forming pellets of the powdered product at high pressure, sintering the pellets at a temperature between 500 and 1000°C for between one half and three hours, and subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for between one half and five hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product.

EP 0 275 343 A1

# NEW SUPERCONDUCTIVE COMPOUNDS OF THE $K_2NiF_4$ STRUCTURAL TYPE HAVING A HIGH TRANSITION TEMPERATURE, AND METHOD FOR FABRICATING SAME

## Field of the Invention

The invention relates to a new class of superconductors, in particular to compounds of the  $K_2NiF_4$  type of structure having superconductor properties below a relatively high transition temperature, and to a method for manufacturing those compounds.

## Background of the Invention

Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials: About a quarter of the elements and over 1000 alloys and compounds have been found to be superconductors. Superconductivity is considered a property of the metallic state of the material, in that all known superconductors are metallic under the conditions that cause them to superconduct. A few normally non-metallic materials, for example, become superconductive under very high pressure, the pressure converting them to metals before they become superconductors.

Superconductors are very attractive for the generation and energy-saving transport of electrical power over long distances, as materials for forming the coils of strong magnets for use in plasma and nuclear physics, in nuclear resonance medical diagnosis, and in connection with the magnetic levitation of fast trains. Power generation by thermonuclear fusion, for example, will require very large magnetic fields which can only be provided by superconducting magnets. Certainly, superconductors will also find application in computers and high-speed signal processing and data communication.

While the advantages of superconductors are quite obvious, the common disadvantage of all superconductive materials so far known lies in their very low transition temperature (usually called the critical temperature  $T_c$ ) which is typically on the order of a few degrees Kelvin. The element with the highest  $T_c$  is niobium (9.2 K), and the highest known  $T_c$  is about 23 K for  $Nb_3Ge$  at ambient pressure.

Accordingly, most known superconductors require liquid helium for cooling and this, in turn, requires an elaborate technology and as a matter of principle involves a considerable investment in cost and energy.

It is, therefore, an object of the present inven-

tion to propose compositions for high- $T_c$  superconductors and a manufacturing method for producing compounds which exhibit such a high critical temperature that cooling with liquid helium is obviated so as to considerably reduce the cost involved and to save energy.

The present invention proposes to use compounds having a layer-type structure of the kind known from potassium nickel fluoride  $K_2NiF_4$ . This structure is in particular present in oxides of the general composition  $RE_2TM.O_x$ , wherein RE stands for the rare earths (lanthanides) and TM stands for the so-called transition metals. It is a characteristic of the present invention that in the compounds in question the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group, and that the oxygen content is at a deficit.

For example, one such compound that meets the description given above is lanthanum copper oxide  $La_2CuO_4$  in which the lanthanum which belongs to the IIIB group of elements is in part substituted by one member of the neighboring IIA group of elements, viz. by one of the alkaline earth metals (or by a combination of the members of the IIA group), e.g., by barium. Also, the oxygen content of the compound is incomplete such that the compound will have the general composition  $La_{2-x}Ba_xCuO_{4-y}$ , wherein  $x \leq 0.3$  and  $y < 0.5$ .

Another example for a compound meeting the general formula given above is lanthanum nickel oxide wherein the lanthanum is partially substituted by strontium, yielding the general formula  $La_{2-x}Sr_xNiO_{4-y}$ . Still another example is cerium nickel oxide wherein the cerium is partially substituted by calcium, resulting in  $Ce_{2-x}Ca_xNiO_{4-y}$ .

The following description will mainly refer to barium as a partial replacement for the lanthanum in a  $La_2CuO_4$  compound because it is the Ba-La-Cu-O system which is, at least at present, the best understood system of all possible. Some compounds of the Ba-La-Cu-O system have been described by C. Michel and B. Raveau in Rev. Chim. Min. 21 (1984) 407, and by C. Michel, L. Er-Rakho and B. Raveau in Mat. Res. Bull., Vol. 20, (1985) 667-671. They did, however, not find nor try to find, superconductivity.

Experiments conducted in connection with the present invention have revealed that high- $T_c$  superconductivity is present in compounds where the rare earth is partially replaced by any one or more of the other members of the same IIA group of elements, i.e. the other alkaline earth metals. Ac-



tually, the  $T_c$  of  $\text{La}_2\text{CuO}_{4-y}$  with  $\text{Sr}^{2+}$  is higher and is superconductivity-induced diamagnetism larger than that found with  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ .

As a matter of fact, only a small number of oxides is known to exhibit superconductivity, among them the Li-Ti-O system with onsets of superconductivity as high as 13.7 K, as reported by D.C. Johnston, H. Prakash, W.H. Zachariasen and R. Viswanathan in *Mat. Res. Bull.* 8 (1973) 777. Other known superconductive oxides include Nb-doped  $\text{SrTiO}_3$  and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , reported respectively by A. Baratoff and G. Binnig in *Physics* 108B (1981) 1335, and by A.W. Sleight, J.L. Gillson and F.E. Bierstedt in *Solid State Commun.* 17 (1975) 27.

The X-ray analysis conducted by Johnston et al. revealed the presence in their Li-Ti-O system of three different crystallographic phases, one of them, with a spinel structure, showing the high critical temperature. The Ba-La-Cu-O system, too, exhibits a number of crystallographic phases, namely with mixed-valent copper constituents which have itinerant electronic states between non-Jahn-Teller  $\text{Cu}^{3+}$  and Jahn-Teller  $\text{Cu}^{2+}$  ions.

This applies likewise to systems where nickel is used in place of copper, with  $\text{Ni}^{3+}$  being the Jahn-Teller constituent, and  $\text{Ni}^{2+}$  being the non-Jahn-Teller constituent.

The existence of Jahn-Teller polarons in conducting crystals was postulated theoretically by K.H. Hoock, H. Nickisch and H. Thomas in *Helv. Phys. Acta* 56 (1983) 237. Polarons have large electron-phonon interactions and, therefore, are favorable to the occurrence of superconductivity at high critical temperatures.

Generally, the Ba-La-Cu-O system, when subjected to X-ray analysis reveals three individual crystallographic phases, viz.

- a first layer-type perovskite-like phase, related to the  $\text{K}_2\text{NiF}_4$  structure, with the general composition  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ , with  $x \leq 1$  and  $y \geq 0$ ;
- a second, non-conducting CuO phase; and
- a third, nearly cubic perovskite phase of the general composition  $\text{La}_{1-x}\text{Ba}_x\text{CuO}_{3-y}$ , which appears to be independent of the exact starting composition.

as has been reported in the paper by J.G. Bednorz and K.A. Müller in *Z. Phys. B - Condensed Matter* 64 (1986) 189-193. Of these three phases the first one appears to be responsible for the high- $T_c$  superconductivity, the critical temperature showing a dependence on the barium concentration in that phase. Obviously, the  $\text{Ba}^{2+}$  substitution causes a mixed-valent state of  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  to preserve charge neutrality. It is assumed that the oxygen deficiency,  $y$ , is the same in the doped and undoped crystallites.

Both  $\text{La}_2\text{CuO}_4$  and  $\text{LaCuO}_3$  are metallic conduc-

tors at high temperatures in the absence of barium. Actually, both are metals like  $\text{LaNiO}_3$ . Despite their metallic character, the Ba-La-Cu-O type materials are ceramics, as are the other compounds of the  $\text{RE}_2\text{TM}_2\text{O}_7$  type, and their manufacture more or less follows the known principles of ceramic fabrication. The preparation of a Ba-La-Cu-O compound, for example, in accordance with the present invention typically involves the following manufacturing steps:

- Preparing aqueous solutions of the respective nitrates of barium, lanthanum and copper and coprecipitation thereof in their appropriate ratios.
- Adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates.
- Decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for one to eight hours.
- Pressing the resulting product at a pressure of about 4 kbar to form pellets.
- Re-heating the pellets to a temperature between 500 and 900°C for one half to three hours for sintering.

It will be evident to those skilled in the art that if the partial substitution of the lanthanum by strontium or calcium is desired, the particular nitrate thereof will have to be used in place of the barium nitrate of the example described above. Also, if the copper of this example is to be replaced by another transition metal, the nitrate thereof will obviously have to be employed.

Experiments have shown that the partial contents of the individual compounds in the starting composition play an important role in the formation of the phases present in the final product. While, as mentioned above, the final Ba-La-Cu-O system obtained generally contains the said three phases, with the second phase being present only to a very small amount, the partial substitution of lanthanum by strontium or calcium (and perhaps beryllium) will result in only one phase existing in the final  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  or  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$ , respectively, provided  $x < 0.3$ .

With a ratio of 1:1 for the respective (Ba, La) and Cu contents, one may expect the said three phases to occur in the final product. Setting aside the said second phase, i.e. the CuO phase, whose amount is negligible, the relative volume amounts of the other two phases are dependent on the barium contents in the  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  complex. At the 1:1 ratio and with an  $x \approx 0.02$ , the onset of a localization transition is observed, i.e., the resistivity increases with decreasing temperature, and there is no superconductivity.

With  $x \approx 0.1$  at the same 1:1 ratio, there is a resistivity drop at the very high critical temperature of 35 K.

With a (Ba,La) versus Cu ratio of 2:1 in the starting composition, the composition of the  $\text{La}_2\text{CuO}_4\text{Ba}$  phase, which was assumed to be responsible for the superconductivity, is limited, with the result that now only two phases are present, the  $\text{CuO}$  phase not existing. With a barium content of  $x = 0.15$ , the resistivity drop occurs at  $T_c = 26$  K.

The method for preparing the Ba-La-Cu-O complex involves two heat treatments for the precipitate at an elevated temperature for several hours. In the experiments carried out in connection with the present invention it was found that best results were obtained at  $900^\circ\text{C}$  for a decomposition and reaction period of 5 hours, and again at  $900^\circ\text{C}$  for a sintering period of one hour. These values apply to a ratio 1:1 composition as well as to a 2:1 composition.

For the ratio 2:1 composition, a somewhat higher temperature is permissible owing to the melting point of the composition being higher in the absence of excess copper oxide. Yet it is not possible by high-temperature treatment to obtain a one-phase compound.

Measurements of the dc conductivity were conducted between 300 and 4.2 K. For barium-doped samples, for example, with  $x < 0.3$ , at current densities of  $0.5 \text{ A/cm}^2$ , a high-temperature metallic behavior with an increase in resistivity at low temperatures was found. At still lower temperatures, a sharp drop in resistivity (>90%) occurred which for higher current densities became partially suppressed. This characteristic drop was studied as a function of the annealing conditions, i.e. temperature and oxygen partial pressure. For samples annealed in air, the transition from itinerant to localized behavior was not found to be very pronounced, annealing in a slightly reducing atmosphere, however, led to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop was shifted towards higher values of the critical temperature. Longer annealing times, however, completely destroy the superconductivity.

Cooling the samples from room temperature, the resistivity data first show a metal-like decrease. At low temperatures, a change to an increase occurs in the case of Ca compounds and for the Ba-substituted samples. This increase is followed by a resistivity drop, showing the onset of superconductivity at  $22 \pm 2$  K and  $33 \pm 2$  K for the Ca and Ba compounds, respectively. In the Sr compound, the resistivity remains metallic down to the resistivity drop at  $40 \pm 1$  K. The presence of localization effects, however, depends strongly on alkaline-earth ion concentration and sample preparation, that is to say, annealing conditions and also on the density which have to be optimized. All samples with low

concentrations of Ca, Sr, and Ba show a strong tendency to localization before the resistivity drop occurs.

Apparently, the onset of the superconductivity, i.e. the value of the critical temperature  $T_c$ , is dependent, among other parameters, on the oxygen content of the final compound. It seems that a certain oxygen deficiency is necessary for the material to have a high- $T_c$  behavior. In accordance with the present invention, the method described above for making the  $\text{La}_2\text{CuO}_4\text{Ba}$  complex is complemented by an annealing step during which the oxygen content of the final product can be adjusted. Of course, what was said in connection with the formation of the  $\text{La}_2\text{CuO}_4\text{Ba}$  compound, likewise applies to other compounds of the general formula  $\text{RE}_2\text{TM}_2\text{O}_7\text{AE}$ , such as, e.g.  $\text{Nd}_2\text{NiO}_7\text{Sr}$ .

In the cases where a heat treatment for decomposition and reaction and/or for sintering was performed at a relatively low temperature, i.e. at no more than  $950^\circ\text{C}$ , the final product is subjected to an annealing step at about  $900^\circ\text{C}$  for about one hour in a reducing atmosphere. It is assumed that the net effect of this annealing step is a removal of oxygen atoms from certain locations in the matrix of the  $\text{RE}_2\text{TM}_2\text{O}_7$  complex, thus creating a distortion in its crystalline structure. The  $\text{O}_2$  partial pressure for annealing in this case may be between  $10^{-1}$  and  $10^{-5}$  bar.

In those cases where a relatively high temperature (i.e. above  $950^\circ\text{C}$ ) was employed for the heat treatment, it might be advantageous to perform the annealing step in a slightly oxidizing atmosphere. This would make up for an assumed exaggerated removal of oxygen atoms from the system owing to the high temperature and resulting in a too severe distortion of the system's crystalline structure.

Resistivity and susceptibility measurements, as a function of temperature, of  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ -doped  $\text{La}_2\text{CuO}_4$  ceramics show the same general tendency as the  $\text{Ba}^{2+}$ -doped samples: A drop in resistivity  $\rho(T)$ , and a crossover to diamagnetism at a slightly lower temperature. The samples containing  $\text{Sr}^{2+}$  actually yielded a higher onset than those containing  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ . Furthermore, the diamagnetic susceptibility is about three times as large as for the Ba samples. As the ionic radius of  $\text{Sr}^{2+}$  nearly matches the one of  $\text{La}^{3+}$ , it seems that the size effect does not cause the occurrence of superconductivity. On the contrary, it is rather adverse, as the data on  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  indicate.

The highest  $T_c$ 's for each of the dopant ions investigated occur for those concentrations where, at room temperature, the  $\text{Re}_2\text{TM}_2\text{O}_7$  structure is close to the orthorhombic-tetragonal structural phase transition which may be related to the substantial electron-phonon interaction enhanced by the substitution. The alkaline-earth substitution of

the rare earth metal is clearly important, and quite likely creates TM ions with no  $e_g$  Jahn-Teller orbitals. Therefore, the absence of these J.-T. orbitals, that is, J.-T. holes near the Fermi energy probably plays an important role for the  $T_c$  enhancement.

#### Claims

1) Superconductive compound of the  $RE_2TM.O_x$  type having a transition temperature above 28 K, wherein the rare earth (RE) is partially substituted by one or more members of the alkaline earth groups of elements (AE), and wherein the oxygen content is adjusted such that the resulting crystal structure is distorted and comprises a phase of the general composition  $RE_{2-x}AE_xTM.O_{x-y}$ , wherein TM represents a transition metal, and  $x < 0.3$  and  $y < 0.5$ .

2) Compound in accordance with claim 1, wherein the rare earth (RE) is lanthanum and the transition metal (TM) is copper.

3) Compound in accordance with claim 1, wherein the rare earth is cerium and the transition metal is nickel.

4) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is nickel.

5) Compound in accordance with claim 1, wherein barium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

6) Compound in accordance with claim 1, wherein calcium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

7) Compound in accordance with claim 1, wherein strontium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

8) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is chromium.

9) Compound in accordance with claim 1, wherein the rare earth is neodymium and the transition metal is copper.

10) Method for making superconductive compounds of the  $RE_2TM.O_x$  type, with RE being a rare earth, TM being a transition metal, the compounds having a transition temperature above 28 K, comprising the steps of:

- preparing aqueous solutions of the nitrates of the rare earth and transition metal constituents and of one or more of the alkaline earth metals and coprecipitation thereof in their appropriate ratios;
- adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates;
- decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for a period of

time between one and eight hours;

- allowing the resultant powder product to cool;
- pressing the powder at a pressure of between 2 and 10 kbar to form pellets;

11) Method in accordance with claim 10, wherein the temperature of the pellets to a value between 500 and 1000°C for a period of time between one half and three hours for sintering;

- subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for a period of time between one half and 5 hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product which has a final composition of the form  $RE_{2-x}TM.O_{x-y}$ , wherein  $x < 0.3$  and  $0.1 < y < 0.5$ .

12) Method in accordance with claim 10, wherein the protected atmosphere is pure oxygen.

13) Method in accordance with claim 10, wherein the protected atmosphere is a reducing atmosphere with an oxygen partial pressure between  $10^{-1}$  and  $10^{-5}$  bar.

14) Method in accordance with claim 10, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed at a temperature of 900°C for one hour in a reducing atmosphere with an oxygen partial pressure between  $10^{-1}$  and  $10^{-5}$  bar.

15) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

16) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

17) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein calcium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

17) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein strontium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

18) Method in accordance with claim 10, wherein cerium is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the cerium, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

EP 87 10 0961

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |  |  |
|---|--|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| D, A  | REVUE DE CHIMIE MINERALE, vol. 21, 1984, pages 407-425, Paris, FR; C. MICHEL et al.: "Oxygen intercalation in mixed valence copper oxides related to the perovskites"<br>* page 417, paragraph 2 - page 425 *<br><br>----- | 1  | H 01 L 39/12                                   |
|   |  |  | TECHNICAL FIELDS SEARCHED (Int. Cl. 4)         |
|   |  |  | H 01 L 39/00                                   |
| The present search report has been drawn up for all claims  |  |  |  |
| Place of search<br>BERLIN   |  | Date of completion of the search<br>17-07-1987   | Examiner<br>ROUSSEL A T                        |
| <b>CATEGORY OF CITED DOCUMENTS</b>  |  |  |  |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br><br>A : member of the same patent family, corresponding document |  |

## Appendix B

## Appendix B

# *Solid State Physics*

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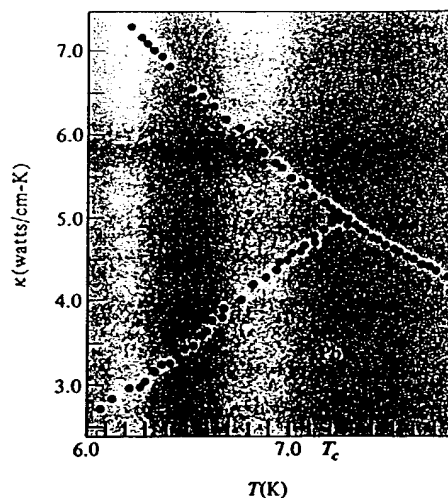
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Figure 34.2

The thermal conductivity of lead. Below  $T_c$  the lower curve gives the thermal conductivity in the superconducting state, and the upper curve, in the normal state. The normal sample is produced below  $T_c$  by application of a magnetic field, which is assumed otherwise to have no appreciable effect on the thermal conductivity. (Reproduced by permission of the National Research Council of Canada from J. H. P. Watson and G. M. Graham, *Can. J. Phys.* 41, 1738 (1963).)



conductivity indicates that even when a superconductor is not carrying an electric current, only a fraction of its conduction electrons are capable of transporting entropy.<sup>15</sup>

### MAGNETIC PROPERTIES: PERFECT DIAMAGNETISM

A magnetic field (provided that it is not too strong) cannot penetrate into the interior of a superconductor. This is most dramatically illustrated by the Meissner-Ochsenfeld effect: If a normal metal in a magnetic field<sup>16</sup> is cooled below its superconducting transition temperature, the magnetic flux is abruptly expelled. Thus the transition, when it occurs in a magnetic field, is accompanied by the appearance of whatever surface currents are required to cancel the magnetic field in the interior of the specimen.

Note that this is not implied by perfect conductivity (i.e.,  $\sigma = \infty$ ) alone, even though perfect conductivity does imply a somewhat related property: If a perfect conductor, initially in zero magnetic field, is moved into a region of nonzero field (or if a field is turned on), then Faraday's law of induction gives rise to eddy currents that cancel the magnetic field in the interior. If, however, a magnetic field were established in a perfect conductor, its expulsion would be equally resisted. Eddy currents would be induced to maintain the field if the sample were moved into a field-free region (or if the applied field were turned off). Thus perfect conductivity implies a time-independent magnetic field in the interior, but is noncommittal as to the value that field must have. In a superconductor, the field is not only independent of time, but also zero.

<sup>15</sup> Presumably the efficacy of the phonons in conducting heat remains undiminished, but this is generally a less important contribution to the thermal conductivity than that of the conduction electrons.

<sup>16</sup> A normal metal is only weakly paramagnetic or diamagnetic (no magnetically ordered metals are superconductors) and an applied magnetic field can penetrate it.

Appendix C

# THEORY OF SUPERCONDUCTIVITY

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## CHAPTER 1

### Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.<sup>1</sup> He was the first to liquefy helium and so to produce temperatures below 10° K. With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about 4.2° K (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g., gold and bismuth, the conductivity remains normal far below even 1° K. Many alloys and compounds can also become superconducting, in particular the frequently used niobium nitride which has a transition temperature as high as 20° K. However, among these latter substances hysteresis phenomena mentioned in the "Introduction" are so much more strongly evident that in testing the present theory we prefer to employ only the "good" superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at a transition temperature  $T_c$ . Actually the resistance-temperature curve does fall more sharply the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

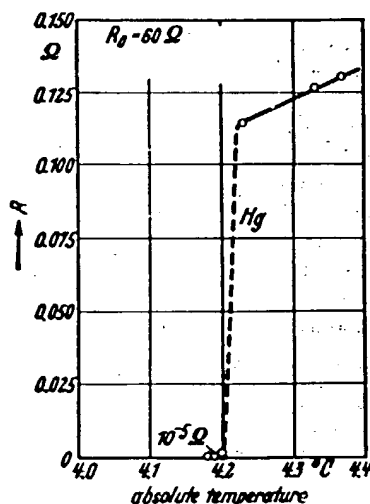


Fig. 1-1. Appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911). The ordinate is the resistance  $R$ ;  $R_0$ , the resistance of solid mercury extrapolated to 0° C, is 60 ohms.

<sup>1</sup>H. Kamerlingh-Onnes, *Commun. Leiden*, 120b, 122b, 124c, (1911).

Apr 24 D.

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# COPPER OXIDE SUPERCONDUCTORS

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PREI

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## PREFACE

The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. The time is now ripe to bring together in one place the results of this research effort so that scientists working in this field can better acquire an overall perspective, and at the same time have available in one place a collection of detailed experimental data. This volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 120 K, from the time of its discovery by Bednorz and Müller in April 1986 until a few months after the award of the Nobel Prize to them in October 1987. During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as  $\text{BiSrCaCuO}$ ,  $\text{LaSrCuO}$ ,  $\text{TlBaCaCuO}$ , and  $\text{YBaCuO}$  has emerged. At the same time there has been a continual debate on the extent to which the BCS theory and the electron-phonon interaction mechanism apply to the new materials, and new theoretical models are periodically proposed. We discuss these matters and, when appropriate, make comparisons with transition metal and other previously known superconductors. Many of the experimental results are summarized in figures and tables.

The field of high-temperature superconductivity is still evolving, and some ideas and explanations may be changed by the time these notes appear in print. Nevertheless, it is helpful to discuss them here to give insights into work now in progress, to give coherence to the present work, and to provide guidance for future work. It is hoped that in the not too distant future the field will settle down enough to permit a more definitive monograph to be written.

Of the transition elements most commonly found in the newer ceramic type superconductors lanthanum is superconducting with a moderately high  $T_c$  (4.88 K for the  $\alpha$  or fcc form and 6.3 for the  $\beta$  or hcp form), yttrium becomes superconducting only under pressure ( $T_c \approx 2$  K for  $110 \leq P \leq 160$  kbar) and copper is not known to superconduct. Studies of the transition temperature of copper alloys as a function of the copper content have provided an extrapolated value of  $T_c = 6 \times 10^{-10}$  K for Cu, which is extremely low. The nontransition elements oxygen and strontium in these compounds do not superconduct, barium only does so under pressure ( $T_c = 1$ –5.4 K for pressures from 55 to 190 kbar), bismuth likewise superconducts only under pressure, and thallium is a superconductor with  $T_c = 2.4$  K. Thus the superconducting properties of the elements are not always indicative of the properties of their compounds, although niobium seems to be an exception, as was mentioned above.

Transition elements combine with a number of other elements to form superconducting materials that sometimes have higher transition temperatures than any of their constituents. These materials may be classified into alloys with the subdivisions solid solutions (with random atomic ordering) and intermetallic compounds or intermetallides (ordered crystallographically), and chemical compounds with the subdivisions ordinary compounds, semiconductors, layered compounds, and polymers. The intermetallides and ordinary compounds provide the highest transition temperatures, with solid solutions and layered compounds also moderately high.

These materials tend to be stoichiometric, and  $T_c$  is often sensitive to it. For example, the gradual approach of  $\text{Nb}_3\text{Ge}$  to stoichiometry raised its measured  $T_c$

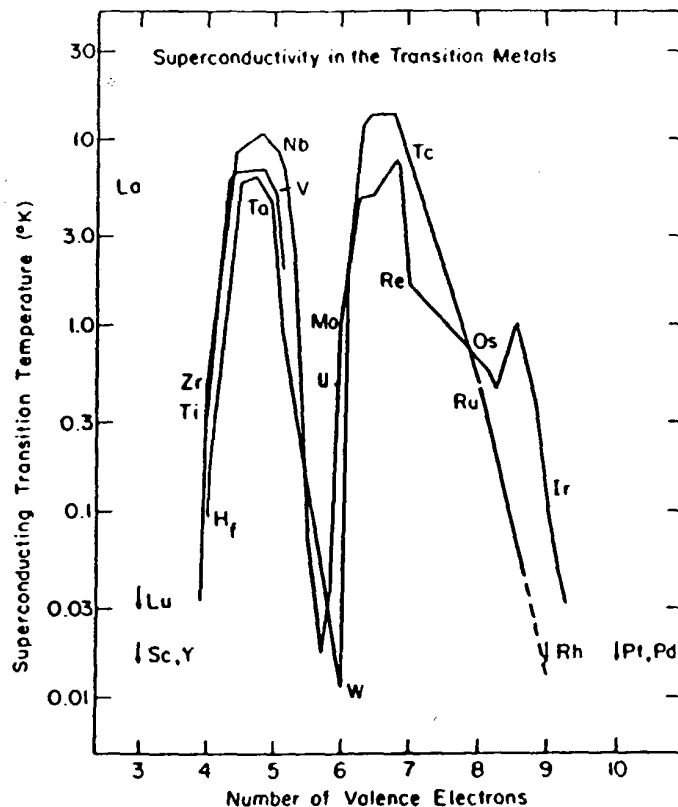


Fig. II-2. The dependence of  $T_c$  on the number of valence electrons  $N_c$  in elements and solid solutions formed by neighboring transition metals. (From Glads, p. 736; see also Hamil and Vonso, pp. 184, 239.)

from 6 to 17 K and finally to 23.2 K. In contrast, there are cases such as  $\text{Cr}_3\text{Os}$ ,  $\text{Cr}_3\text{Ir}$ ,  $\text{Mo}_3\text{Ir}$ ,  $\text{Mo}_3\text{Pt}$ , and  $\text{V}_3\text{Ir}$  in which  $T_c$  is less composition dependent and the highest value does not occur at the stoichiometric composition. This latter case is quite common among the newer superconductors.

Systematic studies of mixed alloys of neighboring transition elements produce a graph similar to Fig. II-2 with intermediate points filled in and the same two maxima. Matthias interpreted these results in terms of the presence of favorable and unfavorable regions of  $N_c$  (Matt1). Amorphous alloys only exhibit one maximum for each series. Other properties such as the electronic specific heat factor  $\gamma$ , the magnetic susceptibility  $\chi$ , the Debye temperature  $\theta_D$ , and the electron-phonon coupling constant  $\lambda$  have dependencies on electron concentration quite similar to the  $T_c$  versus  $N_c$  graph of Fig. II-2.

The highest transition temperatures of the older superconductors were ob-

tetragonal phase, and the metal-to-insulator transition occurs at the tetragonal-to-orthorhombic phase boundary  $x \approx 0.35$  (Matt7, Sleil).

#### D. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller referred to their samples as "metallic, oxygen deficient . . . perovskite like mixed valent copper compounds." Subsequent work has confirmed that the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects.

##### 1. Atom Sizes

In the oxide superconductors Cu replaces the  $Ti^{4+}$  ions ( $0.68 \text{ \AA}$ ) of perovskite, and in most cases retains the  $CuO_2$  layering with two oxygens per copper in the layer. Other cationic replacements tend to be Bi, Ca, La, Sr, Tl, and Y for the larger Ba, forming "layers" containing only one oxygen or none per cation. We see from the following list of ionic radii

|           |                    |        |
|-----------|--------------------|--------|
| $Cu^{2+}$ | $0.72 \text{ \AA}$ |        |
| $Bi^{5+}$ | $0.74 \text{ \AA}$ |        |
| $Y^{3+}$  | $0.94 \text{ \AA}$ |        |
| $Tl^{3+}$ | $0.95 \text{ \AA}$ |        |
| $Bi^{3+}$ | $0.96 \text{ \AA}$ |        |
| $Ca^{2+}$ | $0.99 \text{ \AA}$ | (VI-4) |
| $Sr^{2+}$ | $1.12 \text{ \AA}$ |        |
| $La^{3+}$ | $1.14 \text{ \AA}$ |        |
| $Ba^{2+}$ | $1.34 \text{ \AA}$ |        |
| $O^{2-}$  | $1.32 \text{ \AA}$ |        |

that there are four size groups, with all other cations significantly smaller than the Ba of perovskite. The common feature of  $CuO_2$  layers that are planar or close to planar establishes a fairly uniform lattice size in the  $a, b$  plane. The parameters of the compounds  $LaSrCuO$  ( $a = b = 3.77 \text{ \AA}$ ),  $YBaCuO$  ( $a = 3.83 \text{ \AA}$ ,  $b = 3.89 \text{ \AA}$ ),  $BiSrCaCuO$  ( $a = b = 3.82 \text{ \AA}$ ), and  $TlBaCaCuO$  ( $a = b = 3.86 \text{ \AA}$ ) are all between the ideal fcc oxygen lattice value of  $3.73 \text{ \AA}$  and the perovskite one of  $4.01 \text{ \AA}$ .

Table VI-2 gives the ionic radii of the positively charged ions of various elements of the periodic table. These radii are useful for estimating changes in lattice constant when ionic substitutions are made in existing structures. They also provide some insight into which types of substitutions will be most favorable.

TABL  
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bic, superconducting, and spin-density wave (SDW) regions for the barium compound (Fujit), and data points for the strontium compound (Moret, More8). An alternate phase diagram has been proposed (Ahar1). Alkaline metal contents much larger than those shown on the figure (e.g.,  $x \approx 0.5$ ) can be non-superconducting. The SDW region occurs below the minimum concentration for the onset of superconductivity. Another work (Geise) showed that LaSr(0.04) undergoes a structural phase transition between 180 and 300 K.

### 5. Generation of LaSrCuO Structures

The LaSrCuO tetragonal structures may be visualized as being derived from four LaCuO<sub>3</sub> perovskite unit cells of the type illustrated in Fig. VI-1 stacked one above the other along the  $z$  or  $c$  axis. To generate La<sub>2</sub>CuO<sub>4</sub> in the K<sub>2</sub>NiF<sub>4</sub> structure the layers of CuO<sub>2</sub> atoms on the  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$  levels of this four-cell stacking are removed, La and O are interchanged on two other layers, and the middle layer Cu atom is shifted from the edge to the center point ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) of the unit cell. Then the cell is compressed vertically from 14.9 to 13.2 Å (Table VI-4) to take up the space formerly occupied by the removed CuO<sub>2</sub> layers. Finally, the lanthanums along the  $c$  axis and the oxygens along the side edges are shifted vertically to accommodate the new atom arrangement.

To generate La<sub>2</sub>CuO<sub>4</sub> with the Nd<sub>2</sub>CuO<sub>4</sub> arrangement from this same four-cell stacking all of the oxygens on the vertical edges are removed, and two lanthanums are moved to edge sites. Copper is handled the same way as before, so in both cases the generated structure lacks two CuO<sub>2</sub> layers.

### 6. Layering Scheme of LaSrCuO

When we described the LaSrCuO structures we left out what is perhaps their most important characteristic, namely, their layered aspect. Lanthanum copper oxide may be looked upon as consisting of Cu-O layers of square-planar coordinated copper ions with lanthanum and O(2)-type oxygen ions populating the spaces between the layers. These Cu-O layers are stacked equally spaced, perpendicular to the  $c$  axis, as shown in Fig. VI-7, and their oxygens are aligned along the  $c$  axis, as indicated by the vertical dotted line on the left side of the figure. The copper ions, on the other hand, are not aligned vertically, but rather alternate between (000) and ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) sites in adjacent layers, as illustrated in Figs. VI-5 and VI-7.

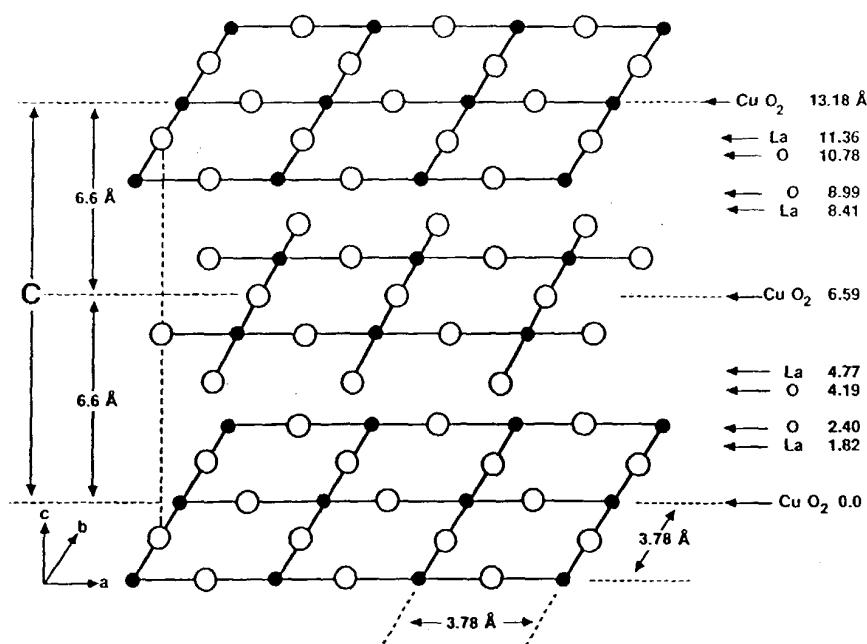
The copper is actually octahedrally coordinated with oxygen, but the Cu-O distance of 1.9 Å in the CuO<sub>2</sub> planes is much less than the vertical distance of 2.4 Å between copper and the oxygens above and below, as shown in Fig. VI-8. When the structure is distorted orthorhombically the Cu-O spacings in both the planes and the  $c$  direction remain quite close to their tetragonal counterparts.

The copper ions and the O(1)-type oxygens in the planes are both in special sites in the tetragonal and orthorhombic forms, in accordance with Eqs. (VI-6) and (VI-9), and as a result the plane is perfectly flat in both cases. When the

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gens are aligned  
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wn in Fig. VI-8.  
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e both in special  
with Eqs. (VI-6)  
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**Fig. VI-7.** Layering scheme of the LaSrCuO superconducting structure. The layers are perpendicular to the  $c$  axis.

structure is tetragonal the square-planar arrangement is also perfect, and of course the planes are perfectly parallel to each other. These characteristics of the planes could influence the superconducting properties.

The copper-oxygen planes are bound together by Cu-O and La-O bonds, as indicated on Fig. VI-5, and Fig. VI-8 shows the spacial arrangement of the CuO<sub>6</sub> octahedra. This figure also makes clear how the copper ions alternate along the *c* axis. The superconducting properties are probably less influenced by the way the planes are bound together than by the internal characteristics of the planes themselves.

## F. YTTRIUM-BARIUM-COPPER OXIDE

The YBaCuO compounds such as  $\text{Y}_{1-x}\text{Ba}_x\text{Cu}_3\text{O}_{7-\delta}$ , like their LaSrCuO counterparts, come in tetragonal and orthorhombic varieties, and both will be described in turn. Then we will show how to generate the structures from their perovskite prototypes, we will explain the layering scheme, and finally related defect structures will be discussed.



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|-----------------|-------------|----------------------|---------------------|
| 08/303,561      | 09/09/94    | REDMONZ              | J Y0987074BY        |

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| ART UNIT | PAPER NUMBER |
|----------|--------------|
|----------|--------------|

1105

DATE MAILED: 05/27/97

*DUE 8/27/97  
FINAL*

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

IBM  
YORKTOWN  
JUN -2 12:38 '97

# Office Action Summary

Application No.  
**08/303,561**

Applicant(s)  
**Bednorz et al.**

Examiner  
**Douglas J. McGinty**

Group Art Unit  
**1105**



☒ Responsive to communication(s) filed on 2-18-97 and 3-7-97

☒ This action is **FINAL**.

☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11; 453 O.G. 213.

A shortened statutory period for response to this action is set to expire 3 month(s), or thirty days, whichever is longer, from the mailing date of this communication. Failure to respond within the period for response will cause the application to become abandoned. (35 U.S.C. § 133). Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

## Disposition of Claims

☒ Claim(s) 24-26, 86-90, and 96-128 is/are pending in the application.

Of the above, claim(s) \_\_\_\_\_ is/are withdrawn from consideration.

☐ Claim(s) \_\_\_\_\_ is/are allowed.

☒ Claim(s) 24-26, 86-90, and 96-128 is/are rejected.

☐ Claim(s) \_\_\_\_\_ is/are objected to.

☐ Claims \_\_\_\_\_ are subject to restriction or election requirement.

## Application Papers

☐ See the attached Notice of Draftsperson's Patent Drawing Review, PTO-948.

☐ The drawing(s) filed on \_\_\_\_\_ is/are objected to by the Examiner.

☐ The proposed drawing correction, filed on \_\_\_\_\_ is ☐ approved ☐ disapproved.

☐ The specification is objected to by the Examiner.

☐ The oath or declaration is objected to by the Examiner.

## Priority under 35 U.S.C. § 119

☒ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☒ All ☐ Some\* ☐ None of the CERTIFIED copies of the priority documents have been  
☐ received.

☒ received in Application No. (Series Code/Serial Number) 08/053,307

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

\*Certified copies not received: \_\_\_\_\_

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

## Attachment(s)

☐ Notice of References Cited, PTO-892

☐ Information Disclosure Statement(s), PTO-1449, Paper No(s). \_\_\_\_\_

☐ Interview Summary, PTO-413

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

--- SEE OFFICE ACTION ON THE FOLLOWING PAGES ---



## DETAILED ACTION

1. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action. The rejections and objections, if any, from the previous Office Action have been withdrawn if not repeated in this Office Action.

2. It is requested that this Examiner be notified of all pending, related applications.<sup>1</sup> That notice need not be in a PTO form - 1449, however.<sup>2</sup>

### *Status of the Claims*

3. Claims 24-26, 86-90, and 96-128 are pending. Claims 109-113 were filed on October 17, 1996 (#57) but were found to be non-responsive in the January 8, 1997 Office Action (#58). The applicants filed a fully responsive amendment with newly added claims 114-128 on February 18, 1997 and a Substitute Amendment on March 7, 1997 (#59). This Office Action addresses the amendments and remarks made in that March 7, 1997 Substitute Amendment.

### *Priority*

4. Acknowledgment is made of applicant's claim for priority under 35 U.S.C. § 119. The certified copy has been filed in parent application, Serial No. 08/053,307, filed on April 23, 1993 as paper no. 28.

a. However, a review of that certified copy, which is in English, indicates that it does not support the present assertion of priority. Support is not found in that certified copy for the invention as presently claimed. See MPEP 201.13 et seq. and 201.14 et seq.

b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The applicants quote some passages out of the priority document and argue that the present

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<sup>1</sup> See MPEP 2001.06(b).

<sup>2</sup> See MPEP 901.03.

claims are fully based that document. Nevertheless, that priority document is not deemed to provide basis for the following limitations found in the present claims:

i. The limitations "a composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen", as found in claim 86 (lines 2-4). The certified priority document may provide basis for the formula  $RE_2TM.O_4$  at p. 2, para. 4, but the claimed composition is deemed to be much broader than that formula.

ii. The limitation "non-stoichiometric amount of oxygen", as found in claim 86 (line 6). Basis may be seen for an oxygen deficit at p. 2, para. 4, but no such basis is seen for the more general limitation of "a nonstoichiometric amount of oxygen".

iii. The limitation "a composition exhibiting a superconductive state", as found in claim 88 (line 2), wherein the composition is a "(transition) metal oxide", as found in claims 24 (lines 1 and 2), 89 and 90. The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but "a composition", "metal oxide", or "transition metal oxide" is deemed to be much broader than the formula  $RE_2TM.O_4$ .

iv. The limitation "a copper-oxide compound", as recited in claim 96 (line 6). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but "a copper-oxide compound" is not deemed to be equivalent to a composition of the formula  $RE_2TM.O_4$ . Basis is not seen in the certified priority document for "a copper-oxide compound" with the breadth of the present claims.

v. The limitation to the effect that "the copper oxide compound includes (including) at least one rare-earth or rare-earth-like element and at least one alkaline-earth element", as recited in claim 97 (lines 3 and 4) and claim 103 (lines 6-8). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but basis is not seen for the more general limitation of "a copper-oxide compound" with a rare-earth (like) element and an alkaline earth element.

vi. The limitation to the effect that "the copper-oxide compound includes at least one element (oxygen) in a nonstoichiometric atomic proportion", as found in claim 101 (lines 2 and 3), 102 (lines 2 and 3), 107 (lines 2 and 3), and 108 (lines 2 and 3). Basis may be seen for

Art Unit: 1105

an oxygen deficit as discussed above, but no such basis is seen for the more general limitation of "a nonstoichiometric atomic proportion".

vii. The limitation as to "the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ ", as found in claim 103 (lines 13, 16, and 17). The critical temperature,  $T_c$ , is discussed throughout that certified priority document, but not  $T_{p=0}$ .

c. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants quote portions out of the priority document and assert that those quoted sections "clearly (support) a much broader composition than the Examiner is claiming it does, and that the priority document, in fact, does support applicant's (sic) claim 86." The fact remains, nevertheless, that the priority document refers to the general formula  $RE_2TM.O_4$  in which the rare earth element (RE) may be partially substituted with a Group IIA metal. That disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to that general formula.

ii. The applicants argue that the disclosure of varying amounts of oxygen in the priority document provides support for earlier priority for the term "non-stoichiometric amount of oxygen". Again, however, that disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to those varying amounts.

iii. The applicants urge that the disclosure in the priority document of the formula  $RE_2TM.O_4$  provides support for their limitations of "transition metal", "copper-oxide compounds", "rare earth or rare earth-like elements", and "alkaline earth element". Again, however, that disclosure in the priority document does not provide support for the broader limitations of the present claims, which do not limit the invention to that formula.

iv. The applicants further "assume that the Examiner agrees with applicant's (sic) statements in their prior response in that the concept of the intercept temperature is well known in the prior art and can be included in claim 103." No basis is seen for that assumption.

As noted in the previous Office Action and repeated above, the term " $T_{p=0}$ " is not found in the priority document. Well known or not, there is no basis for that term in the priority document.

***Claim Rejections - 35 USC § 112***

**5. The specification is objected to under 35 U.S.C. § 112, *first paragraph*, as failing to provide an enabling disclosure commensurate with the scope of the claims.**

a. The present specification is deemed to be enabled only for compositions comprising  $Ba_xLa_{5-x}Cu_5O_y$ . The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases.<sup>3</sup> Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112.<sup>4</sup> Merely reciting a desired result does not overcome this failure.<sup>5</sup> In particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?

b. It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion".<sup>6</sup>

---

<sup>3</sup>See In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218. See also, In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977) (J. Rich).

<sup>4</sup>See In re Cook, 169 USPQ 298, 302; and Cosden Oil v. American Hoechst, 214 USPQ 244, 262.

<sup>5</sup>See In re Corkill, 226 USPQ 105, 1009.

<sup>6</sup>See Brenner v. Manson, 383 US 519, 148 USPQ 689.

c. Claims 24-26, 86-90, and 96-113 are rejected under 35 U.S.C. § 112, *first paragraph*, for the reasons set forth in the objection to the specification.

d. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The additional caselaw and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed.

ii. The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K.

iii. Construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent presently claimed.

(1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the **scope** presently claimed. The claims include formulae which are much broader than the RE-TM-O formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

(a) The present specification actually shows that known forms of "a transition metal oxide", "a composition", and "a copper-oxide compound" do **not** show the

onset of superconductivity at above 26°K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K." Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, non-conducting CuO phase" at p. 14, line 18.

(b) Accordingly, the present disclosure is not deemed to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88, or the "copper-oxide compound" of claim 96.

(3) The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed.

(a) With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-O", per p. 8, line 11) shows "no superconductivity".

(b) With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that **all** of the claims in this application require the critical temperature ( $T_c$ ) to be "in excess of 26°K" or "greater than 26°K".

(c) Consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims. Independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable. Those claims cannot be deemed to be fully enabled.

iv. The applicants also have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^\circ\text{K}$ . Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication,

can make the transition metal oxide compositions encompassed by (the present) claims ...without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art." All three affiants apparently are the employees of the assignee of the present application.

(1) Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.<sup>7</sup>

(2) Those affidavits do not overcome the non-enablement rejection. The present specification discloses *on its face* that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at  $> 26^{\circ}\text{K}$ .

(3) Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made. One may know *now* of a material that superconducts at more than  $26^{\circ}\text{K}$ , but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

(4) It is fully understood that the applicants are the pioneers in high temperature metal oxide superconductivity. The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims.

e. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants quote a statement from part of the previous Office Action and asserts that the "Examiner does not support this statement with any case law citations."

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<sup>7</sup>See In re Lindner, 173 USPQ 356, 358 (CCPA 1972).

(1) That assertion is incorrect. Seven decisions have been cited as providing the legal basis for this determination of non-enablement.<sup>8</sup>

(2) The applicants further "note that the Examiner seemed to have specifically avoided applying (sic) the case law and, consequently, ... applicants take the Examiner's silence as concurrence in the manner that applicants have applied this case law." Apparently, the applicants are referring to their discussion<sup>9</sup> of the caselaw previously cited by this Examiner. Notwithstanding the applicants' commentary on caselaw, the April 15, 1997 Office Action, paper no. 54, sets forth the factual basis for the determination of non-enablement at pp. 5-10.

(3) The applicants still further argues "that the Examiner does not rebut the case law and argument provided by applicants on (pages) 15-25 of their September 29, 1995 amendment which addresses (these issues) in detail." The point remains, nevertheless, that there appears to be a concurrence as to the applicable caselaw. That caselaw speaks for itself. What has been fully addressed in the previous Office Action and repeated above is the factual basis for the determination of non-enablement for the scope of the present invention.

ii. The applicants urge that "their disclosure supports a substantially broader scope than (particular) species." With respect to transition metals, the applicants point to the support in their disclosure and argue that they were enabled for transition metals other than just copper. Again, however, it is noted that high temperature superconductivity is a highly unpredictable art. In view of the record as a whole, it is again determined that one skilled in the art would not have been enabled to practice the presently disclosed invention with transition metals other than copper.

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<sup>8</sup>See footnotes 1-4 in the April 15, 1996 Office Action, paper no. 54. See also, the corresponding sections of this Office Action.

<sup>9</sup>See pp. 12-25 of the September 29, 1995 Amendment, paper no. 50.



iii. The applicants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a whole. If the applicants could not show superconductivity with a  $T_c > 26^\circ\text{K}$  for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made.

iv. The applicants assert that "(b)y the Examiner's statement that these (statements in the affidavits) are conclusionary (sic) the Examiner appears to be placing himself up as an expert in the field of superconductivity" and "respectfully request that the Examiner submit an affidavit in the present application rebutting the position taken by applicants' 3 affiants." Notwithstanding those assertions, this Examiner has determined that those affidavits were insufficient because they were conclusory only, i.e., they lacked particular facts to support the conclusions reached.

v. The applicants argue that the "Examiner has provided no substantial evidence to support this assertion (of non-enabling scope of the invention). It is respectfully requested that the Examiner support (his) assertion with factual evidence and not unsupported statements." Nevertheless, the determination of non-enabling scope is maintained for the reasons of record. This Office Action is deemed to be a complete discussion of all relevant issues raised by the applicants.

**6. Claims 86-87, 96-108, 115, 118, 120, 122, and 123 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.**

a. With respect to claims 86-87 and 96-108, the terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing.

i. The question arises: What is meant by these terms?

ii. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

(1) The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite.<sup>10</sup> It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

(2) The applicants respond that "(a) person of skill in the art would understand (rare earth-like) to mean that a location occupied by a rare earth element can also be occupied by another element which would have chemical properties similar enough to the rare earth elements such that it would fit in to the latter (sic - lattice?) site occupied by the rare earth element." That response does not alleviate the problem, however. Other elements may "fit" into the lattice but they may not necessarily be "rare-earth-like". It is suggested that the same language be changed to -- Group III B --, per p. 7, line 11, of the present specification.

b. Newly added claims 112, 113, 115, 117, 118, 120, 122, and 123 are found to be indefinite for the reasons that follow.

i. In claim 112, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

ii. In claim 113, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

iii. New claim 115, lines 2-4, is indefinite with the language "forming a composition including copper, oxygen and **any** element selected from the group consisting of at least one Group IIA element and an element selected from the group consisting of a rare earth element and a Group IIIB element" (emphasis added). That language is unclear as to whether the Group IIA element must be present along with either the rare earth or Group IIIB element. It is suggested that "any" be changed to -- an -- in line 2.

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<sup>10</sup>See Ex parte Remark, 15 USPQ 2d 1498, 1500 (BPAI 1990); Ex parte Kristensen, 10 USPQ 2d 1701, 1703 (BPAI 1989); Ex parte Attig, 7 USPQ 2d 1092, 1093 (BPAI 1988); and Ex parte Copenhaver, 109 USPQ 118 (POBA 1955).

iv. In claim 117, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

v. In claim 118, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

vi. Claim 120 is unclear the "copper oxide" of line 5 is the "transition metal" and "oxygen" of line 2.

vii. Claim 120, lines 2-4, is indefinite with the language "any element selected from the group consisting of at least one Group IIA element and an element selected from the group consisting of a rare earth element and a Group IIIB element" (emphasis added). That language is unclear as to whether the Group IIA element must be present along with either the rare earth or Group IIIB element. It is suggested that "any" be changed to -- an -- in line 2.

viii. In claim 122, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

ix. In claim 123, line 5, has the terms "layer-type" and "perovskite-like", both of which are indefinite.

x. Claim 123, line 12, has the typographical error of "T T<sub>c</sub>".

c. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants assert "that the Examiner has not responded to applicants' comments which supports applicants' position that a person of skill in the art would understand the terms 'layer-type' and 'perovskite-like' and has just repeated their rejection of the prior Office Action." That assertion is not correct, since April 15, 1996 Office Action, paper no. 54, addressed the applicants' comments at pp. 8 and 9.

ii. The prior Office Action included a proposed amendment to overcome this rejection, which has been repeated above.

*Claim Rejections - 35 USC § 102*

7. Claims 24-26, 86-90, and 96-128 are rejected under 35 U.S.C. § 102(a) as being anticipated by Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article").

a. As discussed in paper no. 20 of the ancestral application, 07/053,307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later than around December 13, 1986, the date samples were tested in the US to show superconductivity. See MPEP 715 et seq. The Asahi Shinbum article was published on November 28, 1986.

b. The reference confirms superconductivity in an oxide compound of La and Cu with Ba having a structure of the so-called perovskite structure. Although the reference fails to teach use of the testing of zero resistance for confirming superconductivity, it inherently must have been used because it is one of two methods used for testing for superconductivity (the other being diamagnetism). Accordingly, the burden of proof is upon the applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference.<sup>11</sup>

c. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The applicants argue that the Sung II Park Affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of the affiant's recollection, or no later than November 15, 1986. The documentary evidence is not deemed to support that argument, however. See MPEP 715.07.

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<sup>11</sup>See In re Brown, 173 USPQ 685, 688; In re Best, 195 USPQ 430; and In re Marosi, 218 USPQ 289, 293.

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(1) Plots of those measurements are missing. See the Chang C. Tsuei Affidavit of March 30, 1988, para. 6. A hand-drawn diagram with the indication of vacuum pumping on November 9, 1988 also is not deemed to show that the measurements were taken.

(2) Moreover, the other evidence in the record appears to show that high temperature superconductivity was not attained in this country as of November 9 or 15, 1986. The March 30, 1986 Declaration of Richard L. Greene includes a series of cablegrams sent by Dr. Greene to the applicants in Zurich, Switzerland as Exhibit B. On both November 11, 1986 and November 14, 1986, Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperatures of 4-35°K. Exhibit C has pages dated December 1, 1986 on, and Exhibit D, which actually has plots of resistance vs. temperature, has an earliest date of December 3, 1996.

ii. The applicants assert that the Asahi Shinbum article reports a third party's confirmation of their original discovery. That assertion appears to be correct, but the article still is deemed to be prior art under 35 USC 102(a).

(1) It should be noted again, however, that the applicants' discovery was not originally made in this country and that they cannot show an earlier date than December 1986 for their invention in this country. The Asahi Shinbum article was published on November 28, 1986.

(2) The applicants cite four decisions<sup>12</sup> which do not directly apply to the present facts.

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<sup>12</sup>One decision is cited in the January 4, 1996 Supplementary Response, paper no. 51: In re Katz, 215 USPQ 14 (CCPA 1982). Three decisions are cited in the April 11, 1996 Supplementary Response, paper no. 53: Andrews v. Hovey, 123 US 267 (1887); Ex parte Lemieux, 115 USPQ 148 (POBA 1957); and Ex parte Powell and Davies, 37 USPQ 285 (POBA 1938).

(a) The In re Katz<sup>13</sup> decision held that an applicant may overcome an article as 35 USC 102(a) prior art by showing that the applicant was a co-author and that the other co-authors were under the direction and control of the applicant. Here, however, the applicants were neither co-authors in the Asahi Shinbum article nor did they exercise direction and control over the work reported in that article.

(b) The Andrews v. Hovey<sup>14</sup> decision involved a grace period which is now codified in 35 USC 102(b). The present case involves a printed publication as prior art under 35 USC 102(a).

(c) The Ex parte Powell and Davies<sup>15</sup> decision held that an applicant's own foreign patent which issued within the grace period cannot be used against him or her, and the Ex parte Lemieux<sup>16</sup> decision applied that reasoning to an applicant's own article published in another country. Again, the present applicants had no part in the writing of the Asahi Shinbum article.

(3) The present facts may raise a novel issue of law.<sup>17</sup> The applicants were the first to develop the presently claimed invention, but the earliest date they can show for

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<sup>13</sup>See In re Katz, *supra*, 215 USPQ at 17, 18. See also, MPEP 716.10.

<sup>14</sup>See Andrews v. Hovey, *supra*.

<sup>15</sup>See Ex parte Powell and Davies, *supra*, 37 USPQ at 285, 286.

<sup>16</sup>See Ex parte Lemieux, *supra*, 115 USPQ at 149. See also, MPEP 715.01(c).

<sup>17</sup>The applicants did not cite In re Mathews, 161 USPQ 276, 277-279 (CCPA 1969), which held that an applicant may overcome a patent as prior art under 35 USC 102(e) with evidence that the applicant provided the knowledge for the disclosure in that patent. By contrast, the present facts involve prior art under 35 USC 102(a) with a publication date before the invention was in this country.

that invention in this country is December of 1986.<sup>18</sup> The Asahi Shinbum article was published in November of 1986 and describes the development of superconductivity with an oxide of La, Ba, and Cu having a perovskite structure by a third party, but that article apparently indicates that the third party was confirming the discovery of the present applicants. Notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article still is deemed to be prior art under 35 USC 102(a), which the applicants have not been able to overcome with a showing of an earlier date in this country or a showing of their direction and control over the work done by that third party.

d. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive.

i. The applicants argue that "Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting (the inventors) on or about October 16, 1986. When these samples came into the United States since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date." As stated before repeated above, however, the applicants were unable to show the attainment of superconductivity any earlier than December 3, 1986 in this country. Again, the present invention is directed to the method of superconducting electricity. That *method* apparently was not reduced to practice before December 3, 1986.

ii. The applicants further urge that they have shown clear diligence from before November 28, 1986 until actual reduction at or around December 3, 1986. Nevertheless, the actual reduction in this country is deemed to have occurred on December 3, 1986, which is after the publication date for the reference.

iii. The applicants assert that they should be entitled to a one-year grace period for their own published invention, but this prior art rejection is based on 35 USC 102(a) because the author of that reference is a different inventive entity.

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<sup>18</sup>The applicants' proposed priority date for the EPO application is January 23, 1987, which is after the December 1986 dates show by the Richard L. Greene Affidavit.

iv. The applicants argue: "If one would follow the rationale of the Examiner, if an applicant publishes an article and some other third party reports that same result prior to applicant's filing of a patent application which is subsequently filed within one year of applicant's own publication (, the) reporting of applicant's work by the third party would be prior art against applicant's application. Such a result would deny (the applicant) the one year grace period provided under 35 USC 102(b)." The applicants' argument is duly noted, but again, it is further noted that the reference is prior art under 35 USC 102(a). The reference is not just a republication of the applicants' article. Instead, the reference is the reporting of someone else's work which confirms the applicants' work. The applicants also are not able to show a priority date which pre-dates the publication of that reference. Usually, an applicant can establish an earlier priority date with an earlier foreign filing, but the EPO priority document in this case was filed on January 23, 1987, or by earlier conception and diligent reduction to practice, but in this case the invention was made outside of this country.

v. This Office Action is deemed to be a complete discussion of all relevant issues raised by the applicants.

***Claim Rejections - 35 USC § 103***

**8. Claims 24-26, 86-90, and 96-128 are rejected under 35 U.S.C. § 103 as being unpatentable over the Asahi Shinbum article.**

a. The reference is relied upon as set forth in the previous rejection. This reference may differ from the present claims in that it may fail to disclose the presently claimed method of "causing an electric current to flow in the superconductor element". It was notoriously well-known in the art of superconductors that a method of utilizing superconductive materials was to cause an electric current to flow in the material while it is cooled below its transition temperature. See MPEP 706.02(a). Accordingly, it would have been well within the purview of one of ordinary skill to use the present claimed method with the materials disclosed by the reference. One would have been motivated to cool the material of the reference to below the transition temperature and cause electric current to flow in the material to provide electricity without resistance. Accordingly, the present claims are unpatentable in view of the prior art of record.



b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The Asahi Shinbum article is deemed to be prior art under 35 USC 102(a) for the reasons discussed above.

c. Applicants' arguments filed March 7, 1997 (#59) have been fully considered but they are not persuasive. The applicants' arguments have been fully discussed above.

***Possibly Allowable Subject Matter***

9. It is noted that the applicants were awarded the Nobel Prize for their work in this area. The record is not deemed to indicate, however, that the Asahi Shinbum article was predicated by the applicants' earlier conception and/or reduction to practice *in this country*. The presently claimed invention also is non-enabling and indefinite for the reasons set forth above.

10. To possibly overcome the above rejections, the following amendments are suggested:

a. 129 (New). A method comprising the steps of:

forming a composition of the formula  $Ba_xLa_{5-x}Cu_5O_y$ , wherein x is from about 0.75 to about 1 and y is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical current through said composition while said metal oxide phase is in said superconducting state.

b. Cancel claims 24-26, 86-90, and 96-128.

11. The following is an Examiner's statement of reasons for the indication of possibly allowable subject matter:

a. The Asahi Shinbum article teaches in general that perovskite-like compounds of La, Cu, and Ba have a  $T_c$  of 30°K, but that article apparently does not teach the particular formula

in the amendment suggested above. The examples in the present specification are deemed to show criticality for that formula in that suggested amendment.

b. Support for the proposed amendment is found at p. 20, line 1, through p. 25, line 5, and in Figure 3.

c. This indication of possibly allowable subject matter is subject to further consideration and review.

### *Conclusion*

12. **THIS ACTION IS MADE FINAL.** The new grounds of rejection, if any, were necessitated by an Amendment.<sup>19</sup> Applicant is reminded of the extension of time policy as set forth in 37 C.F.R. § 1.136(a).

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS FINAL ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS ACTION. IN THE EVENT A FIRST RESPONSE IS FILED WITHIN TWO MONTHS OF THE MAILING DATE OF THIS FINAL ACTION AND THE ADVISORY ACTION IS NOT MAILED UNTIL AFTER THE END OF THE THREE-MONTH SHORTENED STATUTORY PERIOD, THEN THE SHORTENED STATUTORY PERIOD WILL EXPIRE ON THE DATE THE ADVISORY ACTION IS MAILED, AND ANY EXTENSION FEE PURSUANT TO 37 C.F.R. § 1.136(a) WILL BE CALCULATED FROM THE MAILING DATE OF THE ADVISORY ACTION. IN NO EVENT WILL THE STATUTORY PERIOD FOR RESPONSE EXPIRE LATER THAN SIX MONTHS FROM THE DATE OF THIS FINAL ACTION.

13. All of the references cited in this application indicate the level of skill in the relevant art at the time the invention was made.

14. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Douglas J. McGinty, whose telephone number is (703) 308-3805. The examiner normally can be reached on Monday through Friday from 8:30 A.M. to 5:00 P.M., Eastern time. If *reasonable* attempts to reach the examiner by telephone are unsuccessful, however, the examiner's supervisor, Mr. Paul Lieberman, can be reached at (703) 308-2523. Any inquiry of a general nature or relating to the status of this application should be directed to the

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<sup>19</sup>See MPEP 706.07(a).

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Group receptionist whose telephone number is (703) 308-0661. The fax number for this Group is (703) 305-3600.

May 27, 1997  
303561.4

*Douglas J. McGinty*  
**Douglas J. McGinty**  
**Primary Examiner**  
**Group 1100**

Filing: Amendment, Amendment/Response Transmittal Sheet,  
Certificate of Mailing

PLEASE STAMP & RETURN TO US

in re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No.: 08/303,561 Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office:

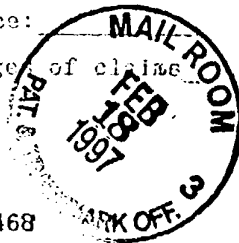
No. of pages of specification \_\_\_\_ : No. of pages of claims \_\_\_\_

No. of sheets of drawings: \_\_\_\_

Declaration is attached to specification.

**All fees** are charged to our Account No. 09-0468

2/10/97



Filing: Amendment, Amendment/Response Transmittal Sheet,  
Certificate of Mailing

PLEASE STAMP & RETURN TO US

in re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No.: 08/303,561 Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office:

No. of pages of specification \_\_\_\_ : No. of pages of claims \_\_\_\_

No. of sheets of drawings: \_\_\_\_

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2/10/97



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: March 6, 1997

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C.

**SUBSTITUTE AMENDMENT**

Sir:

In response to the Office Letter dated January 8, 1997, please consider the following:

**IN THE CLAIMS**

Add claims 114-128.

114. (Added) A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said

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superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

115. (Added) A method comprising the steps of:

forming a composition including copper, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

116. (Added) A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature

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said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

117. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

118. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

119. (Added) A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical



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temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said transitional metal oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

120. (Added) A method comprising the steps of:

forming a composition including a transition metal, oxygen and an element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed transitional metal oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

121. (Added) A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of

26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a transitional metal oxide and at least one element selected from the group consisting of Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

122. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

123. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

124. (Added) A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.

125. (Added) A method comprising the steps of:

forming a composition including copper, oxygen and any element selected from the group consisting of at least one Group II A element and at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

126. (Added) A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of

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26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element.

127. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element;

(b) maintaining the superconductor element at a temperature above

26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

128. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a group II A element, at least one element selected from the group consisting of a rare earth element and at least one element selected from the group consisting of a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature

$T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

**REMARKS**

Claims 24-26, 86-90 and 96 to 128 are in the application.

Claims 113-128 are added by this amendment.

Herein, EA will refer to the Examiner's Action's dated April 15, 1996.

In regard to applicant's claim of priority, in EA paragraphs 3.b.i, 3.b.iii, 3.b.iv and 3.v the Examiner states "the certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ ". It is noted that the Abstract of the priority document refers to "the general formula  $RE_{2-x}AE_xTMO_{4-y}$ , wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two members of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ ." This formula permits no alkaline earth and a varying amount of alkaline earth and rare earths and a varying amount of oxygen. At column 3, lines 20 and 35, there is recited "the Ba-La-Cu-O system" and at line 41 " $La_{2-x}Ba_xDuO_{4-y}$   $x < 1$  and  $y \leq 0$  and at line 44 teaches  $La_{1-x}Ba_xCuO_{3-y}$ ."

The Examiner at page 2 of PA at paragraph 3.b.i states that the priority document does not provide support for "the limitations a composition including a transition metal, a rare earth or rare earth-like elements, an alkaline earth element, an oxygen as found in claim 86". It is noted that in the priority document at column 2, lines 13-19 it is stated that "it is a characteristic of the present invention that in the compounds in question that the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline

earth group and that the oxygen content is at a deficit." It is further noted that at column 2, lines 20-23 it states that "for example, one such compound that meets the description given by this lanthanum copper oxide  $\text{La}_2\text{CuO}_4$  in which the tantalum which belongs to the IIIB group of the elements is in part substituted by one member of the neighboring IIIA group of elements." In the sentence bridging pages 2 and 3 of EA, the Examiner states that "the certified priority document may provide a basis for formula  $\text{RE}_2\text{TM.O}_4$  at P.2, para. 4, but the claimed composition is deemed to be much broader than that formula." It is clear from the quoted sections of the priority document that the priority document clearly supports a much broader composition than the Examiner is stating that the priority document supports, and that the priority document, in fact, does support applicants' claim 86.

At page 3, paragraph ii of EA, the Examiner states there is no support for "the limitation 'non-stoichiometric amount of oxygen', as found in claim 86". Applicants submit that the use of the term oxygen deficit is noted by the Examiner at P.2, para. 4 of the priority document and the varying amount of oxygen given in both formulas is sufficient and adequate support for the limitation 'non-stoichiometric' amount of oxygen." In regards to paragraph iii of page 3 of EA, the Examiner states there is no support for "transition metal oxides" as found in claim 24. Claim 24 recites transition metal oxide which is explicitly recited in the priority document, as stated above. Claim 88 is directed to the superconducting material having a transition temperature in excess of  $26^\circ\text{K}$ . Claim 89 depends from claim 88 and recites that "said composition is comprised of a metal oxide." The priority document supports superconducting material containing or comprising a metal oxide. Claim 90 depends from claim 88 and recites "where said composition is comprised of a transition metal oxide, a copper oxide is a transition metal oxide." The published patent application corresponding to the priority document (EPO 0 274 343 A1, 7-27-88) at column 3, line 6 recites Ti as a transition



metal. It is noted that in claim 1 of the EPO published patent application corresponding to the priority document, claim 1 recites the structure  $RE_{2-x}AE_xTM.O_{4-y}$  wherein TM is a transition metal. Claim 2 therein recites copper as the transition metal. Claim 3 therein recites nickel as the transition metal. Claim 8 therein recites chromium as the transition metal. Consequently, a broader class of transition metals other than copper is supported by the priority document.

At paragraph iv, on page 3 of PA, the Examiner states that "the limitation of 'copper-oxide compounds', as recited in claim 96" is not supported by the priority document with regards to which the Examiner states "the certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ ." As noted above, the general formula recited by the Examiner is incorrectly stated and should be stated wherein the quantity of oxygen, of the rare earth element and of an alkaline element is variable. Consequently, the term "a copper-oxide compound" is adequately supported by the priority document.

In paragraph v on page 3 of EA, the Examiner states that "the limitation to the effect that the 'copper-oxide compound' includes (including) at least one rare earth, rare-earth-like element and at least one alkaline-earth element 'as recited in claim 97... at claim 103...' is not supported by the priority document." The Examiner further states "the certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ ". Applicants as stated above respectfully submit the priority document refers throughout and, in particular, in the Abstract to "the general formula  $RE_{2-x}AE_xEM.O_{4-y}$  as stated above which includes a copper-oxide as stated above. The Examiner further states "but basis is not seen for the more general limitation of 'a copper-oxide compound' with a rare-earth (like) element and in alkaline earth element." It is noted that in the priority document, claim 2 refers to lanthanum as the

rare earth; claim 3 refers to cerium as the rare earth; claim 5 refers to barium as a partial substitute for the rare earth; claim 6 refers to calcium as a partial substitute for the rare earth; claim 7 refers to strontium as a partial substitute for the rare earth and claim 9 refers to neodymium as the rare earth. Clearly, priority document teaches barium, calcium, strontium. Consequently, the priority document supports the term rare earth-like since there are other elements other than those commonly referred to as the rare earth which are elements 57-71 which satisfy the teaching of the priority document and of the present application. The Abstract of the priority document refers to "AE as a member of the alkaline earth or a combination of at least two members of that group". Consequently, the priority document clearly supports an alkaline earth element.

At paragraph vi of page 4 of EA, the Examiner asserts that the priority document does not support "a non-stoichiometric atomic proportion" as found in claims 101, 102, 107 and 108. The exemplary general formula recited above which is recited in the priority document clearly shows the oxygen has a variable content and, consequently, is not in stoichiometric proportion. Consequently, the priority document clearly supports the term "non-stoichiometric atomic proportion".

At paragraph vii of page 4 of EA, the Examiner states that the priority document does not support "the limitation as to 'the effectively-zero-bulk resistivity intercept temperature  $T_0$ ', as found in claim 103." Applicants responded to this same comment at page 6 of their response dated September 26, 1995 at pages 4-6 thereof. The Examiner has not commented upon applicant's remarks and has merely repeated what was said in the Examiner's prior Office Action. Applicant's assume that the Examiner agrees with applicant's statements in their prior response in that the concept of the intercept temperature is well known in the prior art and can be included in claim

103.

In view of the remarks herein, the Examiner is respectfully requested to withdraw the objection to applicant's claim for priority under 35 USC 119 based on applicant's priority document.

In paragraph 4 of EA at page 4 thereof, the specification has been objected to under 35 USC 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims. Paragraphs 4.A, 4.B and 4.C on pages 4-5 of the PA are identical to the Examiner's comments in the previous Office Action.

Paragraph 4-C on page 5 of EA rejects claims 24-26, 86-90 and 96-108 under 35 USC 112, first paragraph, for the same reasons set forth in the objection to the specification which is the same as in the Examiner's prior Office Action.

In paragraph 4-D at page 5 of EA, the Examiner states that he has considered applicant's arguments in response to the Examiner's prior Office Action stating that they "have been fully considered but they are not deemed to be persuasive." At paragraph 4.D.i at page 5 of EA, the Examiner states "the additional case law and arguments by the applicants have been newly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it presently claimed." The Examiner does not specifically respond to the specific passage cited from the case law, nor rebut their applicability in the way applicant's have applied them. Consequently, the Examiner's silence is viewed as agreement with applicant's argument.

At paragraph d.ii on page 6 of EA, the Examiner states that "the applicant's quote several passages from their specification at pp. 13-15 of their September 29, 1995 amendment, the issue is the scope of enablement, not support". The Examiner further states "the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use the composition which shows the onset of superconductivity above 26°K." Applicant's respectfully disagree since recitation of examples is part of the support for the scope of enablement. In addition to the examples recited at page 13-15 of applicant's specification, applicants' comments in their September 29, 1995 amendment, at pages 15-25 clearly show that applicant's "disclosure would have taught one skilled in the art how to make and use the composition which shows the onset of superconductivity above 26°K."

At paragraph d.iii on page 6 of EA, the Examiner states "construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent fully claimed." Applicant's respectfully disagree and note that the Examiner has not specifically rebutted applicant's arguments on page 15-25 of applicant's September 29, 1995 amendment. All that the Examiner has said is that "the invention is not deemed to have been fully enabled by the disclosure to the extent fully claimed."

At paragraph d.iii.1 on page 6 of EA, the Examiner states in regard to applicant's argument in their September 29, 1995 amendment that applicant's states their disclosure "lists several species such as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  which they indicate are found in the present disclosure." Applicant's disclosure supports a substantially broader scope than this species. In particular, the Examiner is directed to applicant's Summary of Invention on page 6-9 of applicant's application. There is no requirement that applicants list every possible species that could possibly come within the scope of

applicant's claims. Applicant's broadly teach transition metal oxides which can contain rare earth and alkaline earth elements.

At paragraph D.iii.1.a, at page 6 of EA, the Examiner states "notwithstanding that argument it still does not follow that the invention is fully enabled for the scope presently claimed." Applicant's respectfully disagree for the reasons provided by applicants on page 15-25 of their September 29, 1995 amendment.

At paragraph d.iii.1.b at page 6 of EA, the Examiner refers to the paragraph bridging pages 3 and 4 of applicant's specification. The Examiner states "the present specification actually shows that known forms of 'transition metal oxide' and 'a copper-oxide compound' do not show the onset of superconductivity above 26°. The Examiner then states that "applicants state that the prior art includes a Li-Ti-O system with superconducting onsets as high as 13.7° K." Applicants do not see the relevance of the Examiner's statements. Such a composition would not be included within the claims since applicant's claim covers only compositions having superconductivity above 26°K. Applicant's acknowledge that Ti is a transition metal. The Examiner notes "that disclosure also refers to 'a second non-conducting CuO phase at p. 14, line 18." Applicant's do not understand the significance of this quoted passage is to the Examiner's argument.

At paragraph d.iii.1.c at page 7 of EA, the Examiner states "accordingly, the present disclosure is not deemed to have been fully enabling with respect to the 'transition metal oxide' of claim 24, the 'composition' of claim 88 or the 'copper-oxide compound' of claim 98." Again, applicant's note applicant's arguments on page 15-25 of their September 29, 1995 amendment. Applicant's, at page 5, line 3 of their specification, refer to transition metal oxides and the sentence bridging pages 5 and 6

to superconducting composition at a  $T_c$  greater than 26°K.

At paragraph d.iii.2 of page 7 of EA, the Examiner states that "the examples of p. 18, lines 1-20, of the present specification further substantiate the finding that the invention is not fully enabled for the scope presently claimed." Applicant's respectfully disagree.

At paragraph d.iii.2.a at page 7 of EA, the Examiner refers to an example in the first paragraph of page 18 of their specification which says at line 10 "and there is no superconductivity." The Examiner appears to be using this paragraph to support the Examiner's assertion that applicant's claims are not enabled by their disclosure. Quite to the contrary, this paragraph supports applicant's assertion that their claims are enabled. Applicant's are providing a broad teaching of how these compositions can be fabricated, by providing a teaching which has not resulted in superconductivity, applicant's are providing a teaching of methods which do lead to examples showing superconductivity. Even if the claims encompass some inoperative examples, this does not render the claims unenabled. Moreover, the claims specifically refer to compounds which are superconducting. Consequently, a sample which is not superconducting is not within the scope of the claim. Applicant's submit that the Examiner is citing fragments of statements from their specification out of context resulting in a misunderstanding of applicant's teaching.

At paragraph d.iii.2.b, at page 7 of EA, the Examiner refers to applicant's example which appears to be in the third paragraph of page 18 of applicant's specification which at line 20 recites  $T_c=26^\circ\text{K}$ . The Examiner then says that applicant's claims require  $T_c$  to be greater than 26°K in what appears to be an attempt to show that applicant's claims are not enabled. Applicants do not believe the

recitation of  $26^{\circ}\text{K}$  in the specification and  $> 26^{\circ}\text{K}$  in the claims has any significance to this argument. Applicant's can amend their claims to say  $\geq 26^{\circ}$  if that's what the Examiner would prefer. Clearly, the temperature consistent with applicant's claims can be infinitesimally close to  $26^{\circ}\text{K}$ .

At paragraph d.ii.2.c at page 7 of EA, the Examiner states "consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims." The Examiner further states "independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable." Applicant's respectfully disagree that the aforementioned examples show that superconductivity is still very unpredictable. The Examiner has taken applicant's examples out of context. These examples are provided as part of the teaching on how to fabricate the claimed invention.

The Examiner further states "those claims cannot be deemed to be fully enabled." Applicants respectfully disagree. It is also noted again that the Examiner has not addressed applicants arguments on page 15-25 of applicants September 29, 1995 amendment.

At paragraph d.iv on page 7 of EA, the Examiner refers to 3 affidavits submitted by applicants. Applicants acknowledge that the 3 affiants are employees of the assignee of the present application. At paragraph d.IV.1 at page 8 of EA the Examiner states "those affidavits do not set forth particular facts to support the conclusions that all superconductors based on applicants' work behave in the same way and that one of skill in the art can make those superconductors without undue experimentation. Conclusionary statements in an affidavit or specification do not

provide the facts or evidence needed for patentability." The referred to affidavits are dated after August 19, 1995 a period of more than 8 years after the present application was filed. Those affidavits refer to developments in the field after the publication of applicants which was cited on page 6 of applicants specification. The statements in the affidavits are not conclusionary but are statements of fact. By the Examiners statement that these are conclusionary the Examiner appears to be placing himself up as an expert in the field of superconductivity. Applicants respectfully request that the Examiner submit an affidavit in the present application rebutting the position taken by applicants 3 affiants.

At paragraph d.iv.2, at page 8 of PA, the Examiner states "those affidavits do not overcome the non-enablement rejection. The present specification discloses on its face that only certain oxides compositions of rare earth, alkaline earth and transition metals made according to the certain steps will superconduct at greater than 26°K." Applicants respectfully disagree with this statement. Applicants' specifications discloses substantially more as applicants have indicated above and as applicants have indicated in their amendment of September 29, 1995. Applicants work clearly started the field of high-temperature superconductivity. Consequently, applicants teaching has enabled this entire field. The Examiners statements to the contrary have no basis in fact.

At paragraph d.iv.3 of page 8 of PA, the Examiner states "those affidavits are not deemed to shed light on the state of the art and enablement at the time the invention was made." Applicant's respectfully disagree. The Examiner has not shown any reason contrary to applicants assertion that the superconducting materials can be made by the methods disclosed by applicant's and as stated by applicant's 3 affiants. Applicant's have objectively enabled their application and their claims. Applicant's



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have pointed to copious locations in their specification which do provide support for applicant's claims.

At paragraph d.iv.4 at page 8 of EA, the Examiner states that "it is fully understood that the applicant's are the pioneers in high temperature metal-oxide superconductivity. The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims." Applicant's respectfully disagree. The Examiner has provided no substantial evidence to support this assertion. It is respectfully requested that the Examiner support their assertion with factual evidence and not unsupported statements.

In view of the remarks herein, the Examiner is respectfully requested to withdraw the objection to the specification under 35 USC 112, first paragraph, and the rejection of claims 24-26, 86-90 and 96-108 under 35 USC 112, first paragraph.

Claims 86-87 and 96-108 have been rejected under 35 USC 112, second paragraph as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant's regard as their invention. Applicant's note that the Examiner has not responded to applicant's comments which supports applicants position that a person of skill in the art would understand the terms "layer-type" and "perovskite-like" and has just repeated their rejection of the prior Office Action. Applicant's respectfully request the Examiner to comment on applicant's prior remarks.

In view of the remarks herein, the Examiner is respectfully requested to withdraw the rejection of claims 86-87 and 96-108 under 35 USC 112, second paragraph.

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Claims 24-26, 86-90 and 96-108 have been rejected under 35 USC 102(a) as being anticipated by Asahi Shinbun Int'l. Satellite Edition (London) November 11, 1986. The Examiner incorrectly gives a date of November 11, 1986 for this article. It is November 28, 1986.

Paragraph 6.a and 6.b of page 10 of EA are essentially the same as in the Examiner's prior action. Applicant's have responded to these paragraphs in their prior response.

In paragraph 6-C at page 10 of EA, the Examiner notes applicant's prior responses and states that they "have been fully considered but they are not deemed to be persuasive." It is noted that in the declaration of co-inventors J.G. Bednorz and K.A. Mueller dated March 21, 1988, mailed into the patent office on June 22, 1988 at paragraph 3 states "On approximately October 16, 1986, we gave Praveen Chaudhari... six samples of the high temperature superconductive ceramic oxide materials that we had described in our aforementioned Z Physik B. publication. Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting with us on or about October 16, 1986." This is evidence that these samples are brought into the United States on or about October 16, 1986. When these samples came into the United States, since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date. It is further noted that the Declaration of Alexis P. Malozenoff signed March 30, 1988 states at paragraph 3, "On or about November 15, 1986, Richard Greene and I travelled to Baltimore for a magnetics conference. During our travel to Baltimore, we discussed Greene's ongoing experiments in high  $T_c$  superconducting samples which he said had been received from Bednorz and Mueller." This is clear evidence that by November 15, 1986, superconducting samples fabricated by applicant's were being

measured in the United States. These samples were inherently superconducting and, consequently, established the reduction to practice in the United States as of that date. The Declaration of Cheng-Chung John Chi dated March 29, 1988 states at paragraph 2, "At a time prior to approximately the middle of November, 1986, Chang C. Tsuei told me a measurement he made on  $T_c$  superconducting material which he said were received from Georg Bednorz and K.A. Mueller, two physicists working for IBM Corporation in Zurich, Switzerland... Chang Tsuei said that he had measured resistivity versus temperature of these samples." This is again further evidence that the Mueller Bednorz superconducting samples were in the United States prior to the middle of November 1986."

At page 11 of EA in the paragraph labelled i, the Examiner states "the applicants argue that Sung Il Park affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of affiants recollection, or no later than November 15, 1986. The document evidence is not deemed to support that argument, however." In the paragraph marked (1) on page 11 of PA, the Examiner states "plots of those measurements are missing. See the Cheng C. Tseui affidavit of March 30, 1988, para. 6." This statement comes directly out of Cheng Tseui's declaration. Notwithstanding, Cheng Tseui's declaration says the measurements were made, that the plots that were taken were missing. The last sentence of this paragraph states "I believe that they may have been inadvertently thrown away when the laboratory was subsequently extensively cleaned." The Examiner further states "a hand-drawn diagram with the indication of a vacuum pumped down on November 9, 1988 also is not deemed to show that the measurements were taken." The Examiner is referring to paragraph 5 of the Cheng Tseui declaration and exhibit C which contains the hand-drawn figure.

At paragraph (2) of page 11 of EA, the Examiner points to cablegrams sent by Dr. Greene to applicants in Zurich which are attached as exhibit B to his declaration. The Examiner states "Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperature 4-35°K." The Examiner fails to note that in the same cablegram dated November 11, 1986, Dr. Greene states "this is not really too surprising given the very broad transition to have found in resistivity and susceptibility." The Examiner acknowledges that "exhibit C has pages dated December 1, 1986 on in exhibit D, which actually has plots and resistance versus temperature dated as early as December 3, 1986." The Examiner is conceding that high  $T_c$  superconductivity was measured on the samples which the very same set of cablegrams and affidavit say were in the United States in the middle of November 1986. Consequently, by the Examiner's own admission, samples which were in the United States were clearly shown to be superconducting as of December 3, 1986. Consequently, the samples that were in the United States as of November 9 were inherently superconducting. It is clear from the same declarations that applicant's were communicating with Dr. Greene. It is noted that Dr. Greene's cablegram dated November 25, 1986 to applicants states he will resume work on the new superconductor and that not much will happen because of the Thanksgiving holiday until the following week. There are cablegrams dated November 26, December 1, December 2, 1986 related to high  $T_c$  superconductivity. Dr. Greene's exhibit C has notebook pages dated December 1, 1986 to December 5, 1986. The December 5, 1986 shows  $T_c$  of 26°K and 30°K. Exhibit D show a plot of R vs. T dated December 8, 1986. Clear reduction to practice is shown and clear diligence is shown from prior to the date of the Asahi Shinbum article. This was clearly done in close correspondence with the applicants. Thus, the facts clearly show applicant's can swear behind the Asahi Shinbum reference.

At paragraph ii on page 11 of EA, the Examiner states "the applicant's assert that the Asahi Shinbum article reports a third parties confirmation of their original discovery. That assertion appears to be correct, but the article is still deemed to be prior art under 35 USC 102(a). At page 12 under paragraph 2, subparagraphs A, B and C, the Examiner made comments in regards to four cases applicant's have cited in support of their position that the Asahi Shinbum article should not be prior art because to hold it as prior art would not afford applicant's the benefit the one year grace period provided them under 35 USC 102(b).

At paragraph 3 on page 13 of EA, applicant's respectfully disagree that the earliest date with which applicant's can show for their invention in this country is December 1986. Numerous affidavits which applicant's have submitted clearly show that applicant's have, in early November 1986, the superconducting compounds which the Examiner admits in applicant's data of December 3, 1986 shown the measurements of critical temperatures. Consequently, the Examiner's statement acknowledges the Examiner's apparent agreement in the fact that the materials were in this country in the middle of November 1986. Applicant's respectfully disagree with the Examiner's statement, "notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article is still deemed to be prior art under 35 USC 102(a), which the applicant's have not been able to overcome with a showing of early date in this country or showing of their direction and control over the work done by the third party." Applicant's note that the Asahi Shinbum article provides no enablement but merely is an assertion of a result achieved which points to applicant's own work which was reported in the article applicant's cite in their application at page 6. Consequently, any description in the Asahi Shinbum article is applicant's own work. If one would follow the rationale of the Examiner, if an applicant publishes an article and

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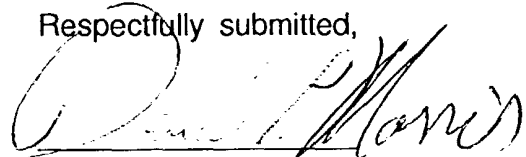
some other third party reports that same result prior to applicant's filing of a patent application, (which is subsequently filed within one year of applicant's own publication) the reporting of applicant's work by the third party would be prior art against applicant's application. Such a result would deny applicant's the one year grace period provided under 35 USC 102(b).

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,



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*Entire Amendment was sent.*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

Date: February 10, 1997

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C.

AMENDMENT

Sir:

In response to the Office Letter dated January 8, 1997, please consider the following:

IN THE CLAIMS

Add claims 114-122.

114. (Added) A method including the steps of forming cor  
therein which exhibits a superconducting state at a critica  
26°K;

maintaining the temperature of said material at a temper  
temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said

*COPY*

*of initially filed  
amendment*

Filing: Amendment, Amendment/Response Trap, Initial Sheet,  
Certificate of Mailing

PLEASE STAMP & RETURN TO US

In re application of: J. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...

Serial No.: 08/303,561 Docket No.: Y0987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification \_\_\_\_: No. of pages of claims \_\_\_\_

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Declaration is attached to specification.

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2/10/97



## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## Amendment/Response Transmittal

In re application of: J. Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS  
FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Transmitted herewith for filing is an Amendment/Response in the above-identified Application.

☐ No additional fee is required.☐ The fee has been calculated as shown below:

| (Col. 1)  |       | (Col. 2)                              | (Col. 3)         | Other Than Small Entity |                     |
|---|-------|---------------------------------------|------------------|-------------------------|---------------------|
| CLAIMS REMAINING<br>AFTER<br>AMENDMENT                            |       | HIGHEST NO.<br>PREVIOUSLY<br>PAID FOR | PRESENT<br>EXTRA | RATE                    | ADDITION-<br>AL FEE |
| TOTAL *   | MINUS | **                                    | =                | x \$22.00=              | \$ 110.00           |
| INDEPENDENT *   | MINUS | ***                                   | =                | x \$80.00=              | \$ 400.00           |
| <input type="checkbox"/> 1ST PRESENTATION OF MULTIPLE DEP. CLAIMS |       |                                       |                  | \$260.00                | \$                  |
|   |       |                                       |                  | TOTAL                   | \$ 510.00           |

\* If the entry in Col. 1 is less than the entry in Col. 2, write "0" in Col. 3.

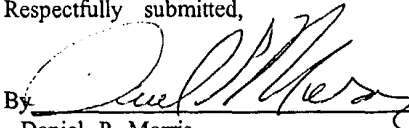
\*\* If the "Highest No. Previously Paid For" IN THIS SPACE is less than 20, write "20" in this space.

\*\*\* If the "Highest No. Previously Paid For" (Total or Independent) is the highest number found from the equivalent box in Col. 1 of a prior amendment or the number of claims originally filed.

☒ Please charge Deposit Account No. 09-0468 any fee necessary to enter this paper.☒ The Commissioner is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 09-0468. A duplicate copy of this sheet is enclosed.☒ Any additional filing fees required under 37 C.F.R. §1.16.☒ Any patent application processing fees under 37 C.F.R. §1.17.Date: February 10, 1997

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Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Date: February 10, 1997

J. Bednorz et al.

Group: 1105

Serial No.: 08/303,561

Examiner: D. McGinty

Filed: September 9, 1994

Docket No. YO987-074BY

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING  
HIGH TRANSITION TEMPERATURE, AND METHODS FOR  
THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)**

I hereby certify that the attached correspondence comprising:

Amendment  
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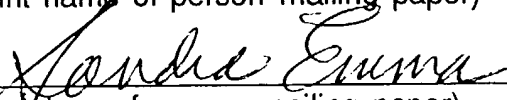
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(Print name of person mailing paper)



(Signature of person mailing paper)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: February 10, 1997

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C.

**AMENDMENT**

Sir:

In response to the Office Letter dated January 8, 1997, please consider the following:

**IN THE CLAIMS**

Add claims 114-122.

114. (Added) A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said

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superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of at least one a rare earth element and a Group III B element.

115. (Added) A method comprising the steps of:

forming a composition including copper, oxygen and any element selected from the group consisting of at least one Group II A element and an element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

116. (Added) A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

117. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

118. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;

(b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

119. (Added) A method including the steps of forming a transition metal oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said

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superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

120. (Added) A method comprising the steps of:

forming a composition including a transition metal, oxygen and any element selected from the group consisting of at least one Group II A element and an element selected from the group consisting of a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

121. (Added) A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature

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said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and at least one element selected from the group consisting of Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element.

122. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.



123. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a transition metal-oxide compound having a layer-type perovskite-like crystal structure, the transition metal-oxide compound including at least one element selected from the group consisting of a Group II A element and at least one element selected from the group consisting of a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

#### **REMARKS**

Claims 24-26, 86-90 and 96 to 113 are in the application.

Herein, EA will refer to the Examiner's Action's dated April 15, 1996.

In regard to applicant's claim of priority, in PA paragraph 3.b.i and in paragraph 3.b.iii and in paragraph 3.b.iv and 3.v the Examiner states "the certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ ". It is noted that the Abstract of the priority document refers to "the second superconductive compounds where oxides of the general formula  $RE_{2-x}AE_xTMO_{4-y}$ , wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two members of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ . This formula permits no alkaline earth and a varying amount of alkaline earth and rare earths and a varying amount of oxygen. At column 3, lines 20 and 35, there is recited "the Ba-La-Cu-O system" and at line 41 " $La_{2-x}Ba_xDuO_{4-y}$ ,  $x < 1$  and  $y \leq 0$  and at line 44 teaches  $La_{1-x}Va_xCuO_{3-y}$ ". The Examiner at page 2 of PA at paragraph 3.b.i states that the priority document does not provide support for "the limitations a composition including a transition metal, a rare earth or rare earth-like elements, an alkaline earth element, an oxygen as found in claim 86". It is noted that in the priority document at column 2, lines 13-19 it is stated that "it is a characteristic of the present invention that in the compounds in question that the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group and that the oxygen content is at a deficit." It is further noted that at column 2, lines 20-23 it states that "for example, one such compound that meets the description given by this lanthanum copper oxide  $La_2CuO_4$  in which the tantalum which belongs to the IIIB group of the elements is in part substituted by one member of the neighboring IIIA group of elements." In the sentence bridging pages 2 and 3 of EA, the Examiner states that "the certified priority document may provide a basis for formula  $RE_2TM.O_4$  at P.2, para. 4, but the claimed composition is deemed to be much broader than that formula." It is clear from the quoted sections of the priority document that the priority document clearly supports a much broader composition than the Examiner is claiming that it does, and that the

priority document, in fact, does support applicant's claim 86.

At page 3, paragraph ii of EA, the Examiner claims there is no support for "the limitation 'non-stoichiometric amount of oxygen', as found in claim 86". Applicants submit that the use of the term oxygen deficit is noted by the Examiner at P.2, para. 4 of the priority document and the varying amount of oxygen given in both formulas in sufficient and adequate support for the limitation 'non-stoichiometric' amount of oxygen." In regards to paragraph iii of page 3 of PA, the Examiner states there is no support for "transition metal oxides" as found in claim 24. Claim 24 explicitly recites transition metal oxide which is explicitly recited in the priority document. Claim 88 is directed to the superconducting material having a transition temperature excess at 26°K. Claim 89 depends from claim 88 and recites that "said composition is comprised of a metal oxide." The priority document support superconducting material containing or comprising a metal oxide. Claim 90 depends from claim 88 and recites "where said composition is comprised of a transition metal oxide, a copper oxide is a transition metal oxide." The issued patent corresponding to the priority at column 3, line 6 recites Ti as a transition metal. [It is noted that in claim 1 of the EPO patent corresponding to the priority document, claim 1 recites the structure  $RE_{2-x}AE_xTM.O_{4-y}$  wherein TM is a transition metal. Claim 2 therein recites copper as the transition metal. Claim 3 therein recites nickel as the transition metal. Claim 8 therein recites chromium as the transition metal. Consequently, a broader class of transition metals other than copper is supported by the priority document.]

At paragraph iv, on page 3 of PA, the Examiner states that "the limitation of 'copper-oxide compounds', as recited in claim 96" is not supported by the priority document with regards to which the Examiner states "the certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ ." As noted above, the

general formula recited by the Examiner is incorrectly stated and should be stated wherein the quantity of oxygen, of the rare earth element and of an alkaline element is variable. Consequently, the term "a copper-oxide compound" is adequately supported by the priority document.

In paragraph v on page 3 of EA, the Examiner states that "the limitation to the effect that the 'copper-oxide compound' includes (including) at least one rare earth, rare-earth-like element and at least one alkaline-earth element 'as recited in claim 97... at claim 103...' is not supported by the priority document." The Examiner further states "the certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ ". Applicants as stated above respectfully submit the Examiner's misrepresenting the priority document which refers throughout and, in particular, in the Abstract to "the general formula  $RE_{2-x}AE_xEM.O_{4-y}$  as stated above which includes a copper-oxide as stated above. The Examiner further states "but basis is not seen for the more general limitation of 'a copper-oxide compound' with a rare-earth (like) element and in alkaline earth element." It is noted that in the priority document, claim 2 refers to lanthanum as the rare earth; claim 3 refers to cerium as the rare earth; claim 5 refers to barium as a partial substitute for the rare earth; claim 6 refers to calcium as a partial substitute for the rare earth; claim 7 refers to strontium as a partial substitute for the rare earth and claim 9 refers to neodymium as the rare earth. Clearly, priority document uses barium, calcium and strontium. Consequently, the priority document supports the term rare earth-like since there are other elements other than those commonly referred to as the rare earth which are elements 57-71 which satisfy the teaching of the priority document and of the present application. The Abstract of the priority document refers to "AE as a member of the alkaline earth or a combination of at least two members of that group". Consequently, the priority document clearly supports an alkaline earth element.

At paragraph vi of page 4 of EA, the Examiner asserts that the priority document does not support "a non-stoichiometric atomic proportion" as found in claims 101, 102, 107 and 108. The exemplary general formula recited above which is recited in the priority document clearly shows the oxygen has a variable content and, consequently, is not in stoichiometric proportion. Consequently, the priority document clearly supports the term "non-stoichiometric atomic proportion".

At paragraph vii of page 4 of EA, the Examiner states that the priority document does not support "the limitation as to 'the effectively-zero-bulk resistivity intercept temperature  $T_0$ ', as found in claim 103." Applicants responded to this same comment at page 6 of their response dated September 26, 1995 at pages 4-6 thereof. The Examiner has not commented upon applicant's remarks and has merely repeated what was said in the Examiner's prior Office Action. Applicant's assume that the Examiner agrees with applicant's statements in their prior response in that the concept of the intercept temperature is well known in the prior art and can be included in claim 103.

In view of the remarks herein, the Examiner is respectfully requested to withdraw applicant's claim for priority under 35 USC 119 based on applicant's priority document.

In paragraph 4 of EA at page 4 thereof, the specification has been objected to under 35 USC 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims. Paragraphs 4.A, 4.B and 4.C on pages 4-5 of the PA are identical to the Examiner's comments in the previous Office Action.

Paragraph 4-C on page 5 of EA rejects claims 24-26, 86-90 and 96-108 under 35 USC 112, first paragraph, for the same reasons set forth in the objection to the specification which is the same as in the Examiner's prior Office Action.

In paragraph 4-D at page 5 of EA, the Examiner states that he has considered applicant's arguments in response to the Examiner's prior Office Action stating that they "have been fully considered but they are not deemed to be persuasive." It is noted that the Examiner makes reference to applicant's case law which is primarily the case law cited by the Examiner in the prior Office Action against applicants, but the Examiner does not specifically respond to the specific passage cited from the case law, nor rebut their applicability in the way applicant's have applied them. Consequently, the Examiner's silence on these issues are taken to mean that the Examiner agrees that these passages from the cited case law are correctly applied by applicants in this application. At paragraph 4.D.i at page 5 of EA, the Examiner states "the additional case law and arguments by the applicants have been newly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it presently claimed." The Examiner does not support this statement with any case law citations. Applicants note that this is not a rebuttal of the applicability of the passages quoted from the case law as applicant's have cited them. Applicant's note that the Examiner seemed to have specifically avoided applying the case law and, consequently, as stated above, applicants take the Examiner's silence as concurrence in the manner that applicant's have applied this case law.

At paragraph d.ii on page 6 of PA, the Examiner states that "the applicant's quote several passages from their specification. At pp. 13-15 of their September 29,

1995 amendment, the issue is the scope of enablement, not support". The Examiner further states "the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use the composition which shows the onset of superconductivity above 26°K." Applicant's believe the Examiner's comments are not appropriate since recitation of examples are part of the support for the scope of enablement. In addition to the examples recited at page 13-15 of applicant's specification, applicants' comments in their September 29, 1995 amendment, at pages 15-25 clearly show that applicant's "disclosure would have taught one skilled in the art how to make and use the composition which shows the onset of superconductivity above 26°K." The Examiner seems to have disregard applicant's comments on pages 15-25.

At paragraph d.iii on page 6 of PA, the Examiner states "construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent fully claimed." Applicant's respectfully disagree and note that the Examiner has not specifically rebutted applicant's arguments on page 15-25 of applicant's September 29, 1995 amendment.

At paragraph d.iii.1 on page 6 of PA, the Examiner states in regard to applicant's argument in their September 29, 1995 amendment that applicant's say their disclosure lists several species such as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  which they indicate are found in the present disclosure." Applicant's respectfully disagree with the tone of the Examiner's statement. Applicant's disclosure supports a substantially broader scope than this species. In particular, the Examiner is directed to applicant's Summary of Invention on page 6-9 of applicant's application. The Examiner seems to confuse scope of invention with specific species recited. There is no requirement that applicants list every possible species that could possibly come within the scope of

applicant's claims. Applicant's broadly teach transition metal oxides.

At paragraph D.iii.1.a, at page 6 of EA, the Examiner states "notwithstanding that argument it still does not follow that the invention is fully enabled for the scope presently claimed." Again, it is noted that the Examiner does not rebut the case law and argument provided by applicants on page 15-25 of their September 29, 1995 amendment which addresses this issue in detail.

At paragraph d.iii.1.b at page 6 of EA, the Examiner refers to the paragraph bridging pages 3 and 4 of applicant's specification. The Examiner states "the present specification actually shows that known forms of 'transition metal oxide' and 'a copper-oxide compound' do not show the onset of superconductivity above 26°. The Examiner then states that "applicants state that the prior art includes a Li-Ti-O system with superconducting onsets as high as 13.7° K." Applicants do not see the relevance of the Examiner's statements. Such a composition would not be included within the claims since applicant's claim covers only compositions having superconductivity above 26°K. Applicant's do not see the relevance of this comment by the Examiner. Applicant's acknowledge that Ti is a transition metal. The Examiner notes "that disclosure also refers to 'a second non-conducting CuO phase at p. 14, line 18." Applicant's do not understand what the significance of reference to the quote at page 14 is to the Examiner's argument.

At paragraph d.iii.1.c at page 7 of EA, the Examiner states "accordingly, the present disclosure is not deemed to have been fully enabling with respect to the 'transition metal oxide' of claim 24, the 'composition' of claim 88 or the 'copper-oxide compound' of claim 98." Again, applicant's note that the Examiner has completely disregarded applicant's arguments on page 15-25 of their September 29, 1995



amendment. Applicant's submit that the Examiner's remarks are not supported by the law and since the Examiner has not specifically rebutted the applicants' arguments which clearly support Applicants' position that these claims are enabled, the consequent conclusion is that the claims are, in fact, enabled.

At paragraph d.iii.2 of page 7 of EA, the Examiner states that "the examples of p. 18, lines 1-20, of the present specification further substantiate the finding that the invention is not fully enabled for the scope presently claimed." Applicant's respectfully disagree.

At paragraph d.iii.2.a at page 7 of EA, the Examiner refers to an example in the first paragraph of page 18 of their specification which says at line 10 "and there is no superconductivity." The Examiner appears to be using this paragraph to support the Examiner's assertion that applicant's claims are not enabled by their disclosure. Quite to the contrary, this paragraph supports applicant's assertion that their claims are enabled. Applicant's are providing a broad teaching of how these compositions can be fabricated, by providing a teaching which has not resulted in superconductivity, applicant's are providing a teaching of methods which do lead to examples showing superconductivity. The Examiner's recitation of this example in this context is, in applicant's view, misleading. Moreover, even if the claims encompass some inoperative examples, this does not render the claims unenabled. Moreover, the claims specifically refer to compounds which are superconducting. Consequently, a sample which is not superconducting is not within the scope of the claim. Applicant's submit that the Examiner is taking fragments of statements from their specification out of context resulting in a misunderstanding of applicant's teaching.

At paragraph d.iii.2.b, at page 7 of EA, the Examiner refers to applicant's

example which appears to be in the third paragraph of page 18 of applicant's specification which at line 20 recites  $T_c = 26^\circ\text{K}$ . The Examiner then says that applicant's claims are directed to " $> 26^\circ\text{K}$ " in what appears to be an attempt to show that applicant's claims are not enabled. Applicant's submit that this is clearly a species argument. Applicant's recitation of  $26^\circ\text{K}$  in the specification and  $> 26^\circ\text{K}$  in the claims has not significance to this argument. Applicant's can amend their claims to say  $\geq 26^\circ$  if that's what the Examiner would prefer. Clearly, the temperature consistent with applicant's claims can be infinitesimally close to  $26^\circ\text{K}$ .

At paragraph d.ii.2.c at page 7 of EA, the Examiner states "consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims." The Examiner further states "independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable." Applicant's respectfully disagree that the aforementioned examples show that superconductivity is still very unpredictable. The Examiner has taken applicant's examples out of context and these examples are provided as part of the teaching on how to fabricate these examples. In particular, the applicant's note that the example given by the Examiner where applicant's state that the  $T_c$  is equal to  $26^\circ\text{K}$  in the specification and applicant's claims say greater than  $26^\circ\text{K}$  is a specious argument.

The Examiner further states "those claims cannot be deemed to be fully enabled." Applicants respectfully disagree. It is also noted again that the Examiner has not addressed applicants arguments on page 15-25 of applicants September 29, 1995 amendment.

At paragraph d.iv on page 7 of EA, the Examiner refers to 3 affidavits submitted

by applicants. Applicants acknowledge that the 3 affiants are employees of the assignee of the present application. At paragraph d.IV.1 at page 8 of EA the Examiner states "those affidavits do not set forth particular facts to support the conclusions that all superconductors based on applicants' work behave in the same way that one of skill in the art can make those superconductors without undue experimentation. Conclusionary statements in an affidavit or specification do not provide the facts or evidence needed for patentability." The referred to affidavits are dated after August 19, 1995 a period of more than 8 years after the present application was filed. Those affidavits refer to developments in the field after publication of applicants which was cited on page 6 of applicants specification. The statements in the affidavits are not conclusionary but are statements of fact. By the Examiners statement that these are conclusionary the Examiner appears to be placing himself up as an expert in the field of superconductivity. Applicants respectfully request that the Examiner submit an affidavit in the present application rebutting the position taken by applicants 3 affiants.

At paragraph d.iv.2, at page 8 of PA, the Examiner states "those affidavits do not overcome the non-enablement rejection. The present specification discloses on its face that only certain oxides compositions of rare earth, alkaline earth and transition metals made according to the certain steps will superconduct at greater than 26°K." Applicants respectfully disagree with this statement. Applicants' specifications discloses substantially more as applicants have indicated above and as applicants have indicated in their amendment of September 29, 1995. Applicants work clearly started the field of high-temperature superconductivity. Consequently, applicants teaching has enabled this entire field. The Examiners statements to the contrary have no basis in fact. Examiners statements have actually no support based on any factual evidence except for the Examiners unsupported statement. Applicants respectfully

request the Examiner to submit an affidavit stating that applicants teaching has not enabled the field of high  $T_c$  superconductors, rebutting applicants arguments and the position taken by the three affidavits submitted by applicants.

At paragraph d.iv.3 of page 8 of PA, the Examiner states "those affidavits are not deemed to shed light on the state of the art and enablement at the time the invention was made." Applicant's respectfully disagree. The Examiner has not shown any reason contrary to applicants assertion that the superconducting materials can be made by the methods disclosed by applicant's and as stated by applicant's 3 affiants. Applicant's have objectively enabled their application and their claims. Applicant's respectfully request that the Examiner provide proof that they have not objectionably enabled the claims. The Examiner has not supported the Examiner's statements that applicant's have not enabled claims. Applicant's have pointed to copious locations in their specification which do provide support for applicant's claims. It is further noted, as noted above, that the Examiner has not rebutted applicant's comments on page 15-25 of applicant's amendment dated September 29, 1995 wherein applicant's point to decisions which support applicant's position that they have enabled their application and their claims.

At paragraph d.iv.4 at page 8 of PA, the Examiner states that "it is fully understood that the applicant's are the pioneers in high temperature metal-oxide superconductivity. The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims." Applicant's respectfully disagree. The Examiner has provided no substantial evidence to support this assertion. It is respectfully requested that the Examiner support their assertion with factual evidence and not unsupported statements.

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In view of the remarks herein, the Examiner is respectfully requested to withdraw the objection to the specification under 35 USC 112, first paragraph, and the rejection of claims 24-26, 86-90 and 96-108 under 35 USC 112, first paragraph.

Claims 86-87 and 96-108 have been rejected under 35 USC 112, second paragraph as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant's regard as their invention. Applicant's note that the Examiner has not responded to applicant's comments which supports applicants position that a person of skill in the art would understand the terms "layer-type" and "perovskite-like" and has just repeated their rejection of the prior Office Action. Applicant's respectfully request the Examiner to comment on applicant's prior remarks.

In view of the remarks herein, the Examiner is respectfully requested to withdraw the rejection of claims 86-87 and 96-108 under 35 USC 112, second paragraph.

In view of the remarks herein, the Examiner is respectfully requested to withdraw the rejection of claims 86-87 and 96-108 under 35 USC 112, second paragraph.

Claims 24-26, 86-90 and 96-108 have been rejected under 35 USC 102(a) as being anticipated by Asahi Shinbum Int'l. Satellite Edition (London) November 11, 1986. The Examiner incorrectly gives a date of November 11, 1986 for this article. It is November 28, 1986.

Paragraph 6.a and 6.b of page 10 of EA are essentially the same as in the Examiner's prior action. Applicant's have responded to these paragraphs in their prior

response.

In paragraph 6-C at page 10 of EA, the Examiner notes applicant's prior responses and states that they "have been fully considered but they are not deemed to be persuasive." It is noted that in the declaration of co-inventors J.G. Bednorz and K.A. Mueller dated March 21, 1988, mailed into the patent office on June 22, 1988 at paragraph 3 states "On approximately October 16, 1986, we gave Praveen Chaudhari... six samples of the high temperature superconductive ceramic oxide materials that we had described in our aforementioned Z Physik B. publication. Praveen Chaudhari brought these samples back to the U.S. when he returned after visiting with us on or about October 16, 1986. This is evidence that these samples are brought into the United States shortly after October 16, 1986. When these samples came into the United States since they were inherently superconductive as claimed, the invention was essentially reduced to practice in the United States on that date. It is further noted that in the Declaration of Alexis P. Malozenoff signed March 30, 1988 states at paragraph 3, "On or about November 15, 1986, Richard Greene and I travelled to Baltimore for a magnetics conference. During our travel to Baltimore, we discussed Greene's ongoing experiments in high  $T_c$  superconducting samples which he said had been received from Bednorz and Mueller." This is clear evidence that by November 15, 1986, superconducting samples fabricated by applicant's were in the United States which were inherently superconducting and, consequently, established the reduction to practice in the United States as of that date. The Declaration of Cheng-Chung John Chi dated March 29, 1988 states at paragraph 2, "At a time prior to approximately the middle of November, 1986, Chang C. Tsuei told me a measurement he made on  $T_c$  superconducting material which he said were received from Georg Bednorz and K.A. Mueller, two physicists working for IBM Corporation in Zurich, Switzerland... Chang Tsuei said that he had measured

resistivity versus temperature of these samples." This is again further evidence that the Mueller Bednorz superconducting samples were in the United States prior to the middle of November 1986."

At page 11 of PA in the paragraph labelled i, the Examiner states "the applicants will argue that Sung Il Park affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of affiants recollection, or no later than November 15, 1986. The document evidence is not deemed to support that argument, however." In the paragraph marked (1) on page 11 of PA, the Examiner states "plots of those measurements are missing. See the Cheng C. Tseui affidavit of March 30, 1988, para. 6." This statement comes directly out of Cheng Tseui's declaration. Notwithstanding, Cheng Tseui's declaration says the measurements were made, that the plots that were taken were missing. The last sentence of this paragraph states "I believe that they may have been inadvertently thrown away when the laboratory was subsequently extensively cleaned." The Examiner further states "a hand-drawn diagram with the indication of a vacuum pumped down on November 9, 1988 also is not deemed to show that the measurements were taken. The Examiner is referring to paragraph 5 of the Cheng Tseui declaration and exhibit C which contains the hand-drawn figure.

At paragraph (2) of page 11 of PA, the Examiner points to cablegram sent by Dr. Greene to applicants in Zurich which are attached as exhibit B to his declaration. The Examiner states "Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperature 4-35°K." The Examiner fails to note that in the same cablegram dated November 11, 1986, Dr. Greene states "this is not really too surprising given the very broad transition to have found in

resistivity and susceptibility." Therefore, the Examiner's conclusion or the way the Examiner characterizes Dr. Greene's cablegrams presents it somewhat inaccurately. The Examiner acknowledges that "exhibit C has pages dated December 1, 1986 on in exhibit D, which actually has plots and resistance versus temperature dated as early as December 3, 1986." The Examiner is conceding that high  $T_c$  superconductivity was measured on the samples which the very same set of cablegrams and affidavit say were in the United States in the middle of November 1986. Consequently, by the Examiner's own admission, samples which were in the United States were clearly shown to be superconducting as of December 3, 1986. Consequently, the samples that were in the United States as of November 9 were inherently superconducting. It is clear from the same declarations that applicant's were communicating with Dr. Greene. It is noted that Dr. Greene's cablegram dated November 25, 1986 to applicants states he will resume work on the new superconductor and that not much will happen because of the Thanksgiving holiday until the following week. There are cablegrams dated November 26, December 1, December 2, 1986 related to high  $T_c$  superconductivity. Dr. Greene's exhibit C has notebook pages dated December 1, 1986 to December 5, 1986. The December 5, 1986 shows  $T_c$  of 26°K and 30°K. Exhibit D show a plot of R vs. T dated December 8, 1986. Clear reduction to practice is shown and clear diligence is shown from prior to the date of the Asahi Shinbum article. This was clearly done in close correspondence with the applicants. Thus, the facts clearly show applicant's can swear behind the Asahi Shinbum reference.

At paragraph ii on page 11 of PA, the Examiner states "the applicant's assert that the Asahi Shinbum article reports a third parties confirmation of their original discovery. That assertion appears to be correct, but the article is still deemed to be prior art under 35 USC 102(a). At page 12 under paragraph 2, subparagraphs A, B and C, the Examiner made comments in regards to four cases applicant's have cited



in support of their position that the Asahi Shinbum article should not be prior art because to hold it as prior art would not afford applicant's the benefit the one year grace period provided them under 35 USC 102(b).

At paragraph 3 on page 13 of PA, applicant's respectfully disagree that the earliest date with which applicant's can show for their invention in this country is December 1986. Numerous affidavits which applicant's have submitted clearly show that applicant's have, in early November 1986, the superconducting compounds which the Examiner admits in applicant's data of December 3, 1986 shown the measurements of critical temperatures. Consequently, even with the Examiner's admitted statement in the Examiner's apparent concurrence in the fact that the materials were in this country in the middle of November 1986. The materials inherently shown in this invention presently claimed. Applicant's respectfully disagree with the Examiner's statement, "notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article is still deemed to be prior art under 35 USC 102(a), which the applicant's have not been able to overcome with a showing of early date in this country or showing of their direction and control over the work done by the third party." Applicant's note that the Asahi Shinbum article provides no enablement but merely is an assertion of a result achieved which points to applicant's own work which was reported in the article applicant's cite in their application at page 6. Consequently, any enablement of the Asahi Shinbum article is applicant's own work. If one would follow the rationale of the Examiner, if an applicant publishes an article and some other third party reports that same result prior to applicant's filing of a patent application which is subsequently filed within one year of applicant's own publication. The reporting of applicant's work by the third party would be prior art against applicant's application. Such a result would deny applicant's the one year grace period provided under 35 USC 102(b).

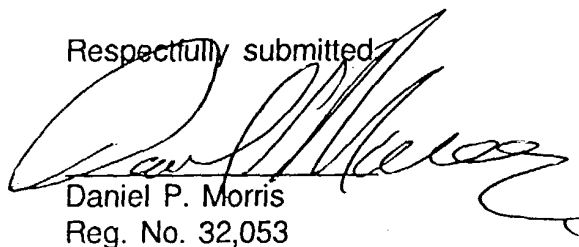
Ser. No. 08/303,561

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Daniel P. Morris", is written over a horizontal line.

Daniel P. Morris  
Reg. No. 32,053

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598  
(914) 945-3216



# UNITED STATES DEPARTMENT OF COMMERCE

## Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. |
|-----------------|-------------|----------------------|---------------------|
| 057/003,504     | 05/07/94    | HEBRONIZ             | 109870746Y          |

DANIEL P MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

109870746Y

|          |
|----------|
| EXAMINER |
|----------|

MC GINTY, D

|          |              |
|----------|--------------|
| ART UNIT | PAPER NUMBER |
|----------|--------------|

1100

DATE MAILED: 01/08/97

DUE 2/8/97

Please find below and/or attached an Office communication concerning this application or proceeding.

# Office Action Summary

Application No.

08/303,561

Applicant(s)

Bednorz et al.

Examiner

Douglas J. McGinty

Group Art Unit

1105



☒ Responsive to communication(s) filed on Oct 17, 1996. That communication is NON-RESPONSIVE.

☐ This action is **FINAL**.

☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11; 453 O.G. 213.

A shortened statutory period for response to this action is set to expire 1 month(s), or thirty days, whichever is longer, from the mailing date of this communication. Failure to respond within the period for response will cause the application to become abandoned. (35 U.S.C. § 133). Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

## Disposition of Claims

☒ Claim(s) 24-26, 86-90, and 96-113 is/are pending in the application.

Of the above, claim(s) \_\_\_\_\_ is/are withdrawn from consideration.

☐ Claim(s) \_\_\_\_\_ is/are allowed.

☐ Claim(s) \_\_\_\_\_ is/are rejected.

☐ Claim(s) \_\_\_\_\_ is/are objected to.

☐ Claims \_\_\_\_\_ are subject to restriction or election requirement.

## Application Papers

☐ See the attached Notice of Draftsperson's Patent Drawing Review, PTO-948.

☐ The drawing(s) filed on \_\_\_\_\_ is/are objected to by the Examiner.

☐ The proposed drawing correction, filed on \_\_\_\_\_ is ☐ approved ☐ disapproved.

☐ The specification is objected to by the Examiner.

☐ The oath or declaration is objected to by the Examiner.

## Priority under 35 U.S.C. § 119

☐ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☐ All ☐ Some\* ☐ None of the CERTIFIED copies of the priority documents have been

☐ received.

☐ received in Application No. (Series Code/Serial Number) \_\_\_\_\_.

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

\* Certified copies not received: \_\_\_\_\_

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

## Attachment(s)

☐ Notice of References Cited, PTO-892

☐ Information Disclosure Statement(s), PTO-1449, Paper No(s). \_\_\_\_\_

☐ Interview Summary, PTO-413

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

--- SEE OFFICE ACTION ON THE FOLLOWING PAGES ---

Art Unit: 1105

**NOTICE OF NON-RESPONSIVE AMENDMENT**

1. The communication filed on October 17, 1996 is non-responsive<sup>1</sup> to the prior Office action because of the reasons that follow:

a. In their October 17, 1996 Amendment, paper no. 57, the applicants state, with parentheses and emphasis added:

In response to the Examiner's interview summary dated May 22, 1996, Applicant's (sic) have added claims 109-113 which correspond to independent claims 24, 86, 88, 96 and 108, respectively. The added claims read the same as these claims **but including the limitations suggested by the Examiner.**

Notwithstanding that statement by the applicants, newly added claims 109-113 do **NOT** correspond to the suggestions made by the Examiner as documented in the Interview Summary dated May 22, 1996, paper no. 55.

i. That Interview Summary states, with emphasis added:

To overcome 112 1st para, rejections, it is suggested that each independent claim be amended to require at least one **each** of a IIA metal, a rare earth or IIIB metal, and copper oxide.

ii. Newly amended claims 109-113 do not "require at least one **each** of a IIA metal, a rare earth or IIIB metal, and copper oxide" (emphasis added). Instead, for instance, claim 109 only requires that "said copper oxide includes at least one element **selected from the group consisting of** a Group II A element, a rare earth element and a Group IIIB element" (emphasis added)." Claims 110-113 each have similar Markush groupings for the II A, rare earth, and III B elements.

---

<sup>1</sup>See MPEP 714.02-714.04.

Art Unit: 1105

b. The October 17, 1996 Amendment, paper no. 57, the applicants further assert:

Claims 24-26, 86-90 and 96-108 have been rejected for essentially the same reasons as in the Office Action dated March 29, 1995. Applicant's (sic) respectfully disagree for the same reasons given in Applicants (sic) response dated September 26, 1995, October 10, 1995 and April 11, 1996, which Applicant's (sic) incorporate herein by reference.

General assertions of patentability are not deemed to be responsive.<sup>2</sup>

2. To be responsive, an amendment must include the following:

a. One or the other approach with respect to newly added claims 109-113:

i. Pursuant to the May 21, 1996 interview, each of claims 109-113 may be amended to recite compositions containing **THREE** components:

- (1) a II A metal;
- (2) a rare earth or III B metal; **AND**
- (3) a copper oxide.

ii. As an alternative, claims 109-113 in their present form may be accompanied by particular arguments to the effect that the same amendments overcome the 35 USC 112 rejections in the previous Office Action.<sup>3</sup>

b. Arguments directed to the particular points raised in the April 15, 1996 Office Action, paper no. 54, with respect to the rejections under 35 USC 112, 102, and 103.

3. Since the response appears to be *bona fide*, but through an apparent oversight or inadvertence failed to provide a complete response, applicant is required to complete the response within a **TIME LIMIT** of **ONE MONTH** from the date of this letter or within the time remaining in the response period of the last Office action, whichever is longer. **NO EXTENSION OF THIS**

---

<sup>2</sup>See 37 CFR 1.111(b).

<sup>3</sup>Each of claims 109-113 still needs to be reviewed for compliance with 35 USC 112 and examined with respect to 35 USC 102 and 103.

Art Unit: 1105

TIME LIMIT MAY BE GRANTED UNDER EITHER 37 CFR 1.136(a) OR (b), but the period for response set in the last office action may be extended up to a maximum of SIX MONTHS.

*Conclusion*

4. Any amendment in response to this Office Action must NOT include any new matter.
5. The applicant or applicants is or are reminded that any evidence to be presented in accordance with 37 CFR 1.131 or 1.132 should be submitted before final rejection in order to be considered timely.
6. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Douglas J. McGinty, whose telephone number is (703) 308-3805. The examiner normally can be reached on Monday through Friday from 8:30 A.M. to 5:00 P.M., Eastern time. If *reasonable* attempts to reach the examiner by telephone are unsuccessful, however, the examiner's supervisor, Mr. Paul Lieberman, can be reached at (703) 308-2523. Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661. The fax number for this Group is (703) 305-3600.

January 3, 1996  
303561.3

*Douglas J. McGinty*  
**Douglas J. McGinty**  
**Primary Examiner**  
**Group 1100**

Filing: Amendment, Amendment/Response Transmittal Sheet,  
Petition and Fee for Three Month Extension of Time, Certificate  
of Mailing

PLEASE STAMP & RETURN TO US

In re application of: J. Bednorz et al.

For: SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION

Serial No. 08/303,561; Docket No. YO987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office:

No. of pages of specification: No. of pages of claims

No. of sheets of drawings:

Specification is attached to specification.

All fees are charged to our Account No. 09-0468

10/15/96

Filing: Amendment, Amendment/Response Transmittal Sheet,  
Petition and Fee for Three Month Extension of Time, Certificate  
of Mailing

PLEASE STAMP & RETURN TO US

In re application of: J. Bednorz et al.

For: SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION

Serial No. 08/303,561; Docket No. YO987-074BY Atty.: DPM

Received in the U.S. Patent & Trademark Office:

No. of pages of specification: No. of pages of claims

No. of sheets of drawings:

Specification is attached to specification.

All fees are charged to our Account No. 09-0468

10/15/96





IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

J. Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

Date: October 15, 1996

Group: 1105

Examiner: D. McGinty

Docket No. YO987-074BY

For: SUPERCONDUCTIVE COMPOUNDS HAVING  
HIGH TRANSITION TEMPERATURE, AND METHODS FOR  
THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)**

I hereby certify that the attached correspondence comprising:

Amendment  
Petition and Fee for Three Month Extension of Time  
Amendment/Response Transmittal Sheet  
Acknowledgement card

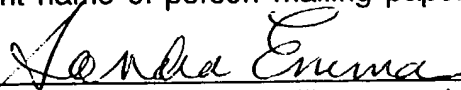
is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

**Commissioner of Patents and Trademarks  
Washington, DC 20231**

on October 15, 1996

Sandra Emma

(Print name of person mailing paper)



(Signature of person mailing paper)

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## Amendment/Response Transmittal

In re application of: J. Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

For: SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS  
FOR THEIR USE AND PREPARATIONCommissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Transmitted herewith for filing is an Amendment/Response in the above-identified Application.

☐ No additional fee is required.☒ The fee has been calculated as shown below:

| (Col. 1)  |       | (Col. 2)                              | (Col. 3)         | Other Than Small Entity |                     |
|---|-------|---------------------------------------|------------------|-------------------------|---------------------|
| CLAIMS REMAINING<br>AFTER<br>AMENDMENT                            |       | HIGHEST NO.<br>PREVIOUSLY<br>PAID FOR | PRESENT<br>EXTRA | RATE                    | ADDITION-<br>AL FEE |
| TOTAL * 26  | MINUS | ** 21                                 | = 5              | x \$22.00=              | \$ 110.00           |
| INDEPENDENT * 10  | MINUS | *** 5                                 | = 5              | x \$80.00=              | \$ 400.00           |
| <input type="checkbox"/> 1ST PRESENTATION OF MULTIPLE DEP. CLAIMS |       |                                       |                  | \$260.00                | \$                  |
|   |       |                                       |                  | TOTAL                   | \$ 510.00           |

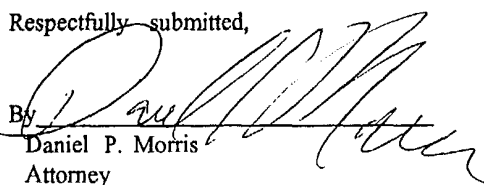
\* If the entry in Col. 1 is less than the entry in Col. 2, write "0" in Col. 3.

\*\* If the "Highest No. Previously Paid For" IN THIS SPACE is less than 20, write "20" in this space.

\*\*\* If the "Highest No. Previously Paid For" (Total or Independent) is the highest number found from the equivalent box in Col. 1 of a prior amendment or the number of claims originally filed.

☒ Please charge Deposit Account No. 09-0468 the fee of \$ 510.00 to enter this paper or any other fee necessary to enter this paper.☒ The Commissioner is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 09-0468. A duplicate copy of this sheet is enclosed.☒ Any additional filing fees required under 37 C.F.R. §1.16.☒ Any patent application processing fees under 37 C.F.R. §1.17.Date: October 15, 1996IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, NY 10598  
Tel. No. (914) 945-3217

Respectfully submitted,

By   
Daniel P. Morris  
Attorney  
Registration No. 32,053

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J. Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

For: SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, AND  
METHODS FOR THEIR USE AND PREPARATION

Group Art Unit: 1105

Examiner: D. McGinty

PETITION AND FEE FOR EXTENSION OF TIME (37 CFR 1.136(a))

Commissioner of Patents and Trademarks  
Washington, DC 20231

Sir:

1. This is a petition for an extension of the time to respond to the Office Letter mailed on April 15, 1996 for a period of 3 months.

2. Applicant is other than a small entity.

3. Extension period and fee:

| <u>(months)</u>                                  | <u>Fee for other than<br/>small entity</u> |
|--|--|
| <input type="checkbox"/> one month               | \$ 110.00                                  |
| <input type="checkbox"/> two months              | \$ 390.00                                  |
| <input checked="" type="checkbox"/> three months | \$ 930.00                                  |
| <input type="checkbox"/> four months             | \$1,470.00                                 |
|  | Fee: \$ <u>930.00</u>                      |

4. An amendment

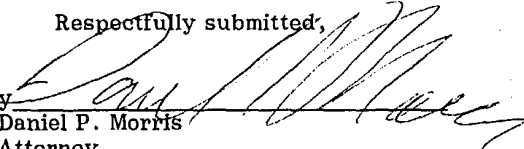
- ☒ is filed herewith.  
☐ has been filed.

5. Fee Payment

- ☒ Charge fee to Deposit Account No. 09-0468 and for any additional fee required to complete the filing or processing of this application or credit any excess fee paid. A duplicate copy of this sheet is enclosed.

Date: October 15, 1996

Respectfully submitted,

By   
Daniel P. Morris  
Attorney  
Registration No. 32,053

Telephone: (914) 945-3217  
Fax: (914) 945-3281

From:  
IBM Corporation  
Intellectual Property Law  
P.O. Box 218  
Yorktown Heights, NY 10598

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

Date: October 15, 1996

Serial No.: 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR  
THEIR USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

AMENDMENT

Sir:

In response to the Office Letter dated April 15, 1996, please consider the following:

IN THE CLAIMS

Add claims 109-113.

109. (Added) A method including the steps of forming copper oxide having a phase therein which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said material at a temperature less than said critical temperature to produce said superconducting state in said phase;

passing an electrical supercurrent through said copper oxide while it is in said superconducting state;

said copper oxide includes at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element.

110. (Added) A method comprising the steps of:

forming a composition including copper, oxygen and any element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element, where said composition is a mixed copper oxide having a non-stoichiometric amount of oxygen therein and exhibiting a superconducting state at a temperature greater than 26°K;

maintaining said composition in said superconducting state at a temperature greater than 26°K; and

passing an electrical current through said composition while said composition is in said superconducting state.

111. (Added) A method including the steps of:

forming a composition exhibiting a superconductive state at a temperature in excess of 26°K;

maintaining said composition at a temperature in excess of 26°K at which temperature said composition exhibits said superconductive state;

passing an electrical current through said composition while said composition is in said superconductive state; and

said composition including a copper oxide and an element selected from the group consisting of Group II A element, a rare earth element and a Group III B element.

112. (Added) A superconductive method for causing electric-current flow in a superconductive state at a temperature in excess of 26°K, comprising:

(a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the composition having a superconductive transition temperature  $T_c$  of greater than 26°K, said superconductive composition includes at least one element selected from the group consisting of a Group II A element, a rare earth element and a Group III B element;

(b) maintaining the superconductor element at a temperature above 26°K and below the superconductor transition temperature  $T_c$  of the superconductive composition; and

(c) causing an electric current to flow in the superconductor element.

113. (Added) A superconductive method for conducting an electric current essentially without resistive losses, comprising:

- (a) providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one element selected from the group consisting of a group II A element, a rare earth element and a Group III B element, the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$ , the transition-onset temperature  $T_c$  being greater than 26°K;
- (b) maintaining the superconductor element at a temperature below the effectively-zero-bulk-resistivity intercept temperature  $T_{\rho=0}$  of the superconductive composition; and
- (c) causing an electric current to flow in the superconductor element.

#### REMARKS

Claims 24-26, 86-90 and 96-108 have been rejected for essentially the same reasons as in the Office Action dated March 29, 1995. Applicant's respectfully disagree for the same reasons given in Applicants response dated September 26, 1995, October 10, 1995 and April 11, 1996, which Applicant's incorporate herein by reference.

In response to the Examiner's interview summary dated May 22, 1996, Applicant's have added claims 109-113 which correspond to independent claims 24, 86, 88, 96 and 108,

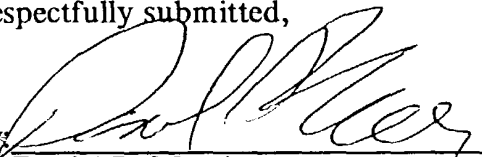
respectively. The added claims read the same as these claims but including the limitations suggested by the Examiner.

In view of the changes to the claims and the remarks herein, the Examiner is respectfully requested to reconsider the above-identified application. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

If the above-identified Examiner's Action is a final Action, and if the above-identified application will be abandoned without further action by applicants, applicants file a Notice of Appeal to the Board of Appeals and Interferences appealing the final rejection of the claims in the above-identified Examiner's Action. Please charge deposit account 09-0468 any fee necessary to enter such Notice of Appeal.

Respectfully submitted,

By   
Daniel P. Morris  
Reg. No. 32,053

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598  
(914) 945-3217





UNITED STATES DEPARTMENT OF COMMERCE  
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Washington, D.C. 20231

|               |             |                       |                     |
|---------------|-------------|-----------------------|---------------------|
| SERIAL NUMBER | FILING DATE | FIRST NAMED APPLICANT | ATTORNEY DOCKET NO. |
|---------------|-------------|-----------------------|---------------------|

08/303,561 09/09/94 BEDNORZ

1 YD927074BY

EXAMINER

MC BINTY, D

11M1/0522

ART UNIT

PAPER NUMBER

DANIEL P MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS N

DATE MAILED: 5  
1105

**EXAMINER INTERVIEW SUMMARY RECORD**

05/22/96

All participants (applicant, applicant's representative, PTO personnel):

(1) Mr. Daniel P. Morris (3) \_\_\_\_\_  
(2) Exam. Douglas J. McINTY (4) \_\_\_\_\_

Date of interview 5-21-96

Type: ☒ Telephonic ☐ Personal (copy is given to ☐ applicant ☐ applicant's representative).

Exhibit shown or demonstration conducted: ☐ Yes ☒ No. If yes, brief description: \_\_\_\_\_

Agreement ☐ was reached with respect to some or all of the claims in question. ☒ was not reached.

Claims discussed: All independent claims (24, 86, 88, 96, 9103)

Identification of prior art discussed: ~~Asahi~~ Asahi Shinbun article

Description of the general nature of what was agreed to if an agreement was reached, or any other comments: TO overcome 112, 1st para, rejections, it is suggested that each independent claim be amended to require at least one each of a II A metal, a rare earth or III B metal, and copper oxide.

(A fuller description, if necessary, and a copy of the amendments, if available, which the examiner agreed would render the claims allowable must be attached. Also, where no copy of the amendments which would render the claims allowable is available, a summary thereof must be attached.)

☒ 1. It is not necessary for applicant to provide a separate record of the substance of the interview.

Unless the paragraph below has been checked to indicate to the contrary, A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION IS NOT WAIVED AND MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW (e.g., items 1-7 on the reverse side of this form). If a response to the last Office action has already been filed, then applicant is given one month from this interview date to provide a statement of the substance of the interview.

☐ 2. Since the examiner's interview summary above (including any attachments) reflects a complete response to each of the objections, rejections and requirements that may be present in the last Office action, and since the claims are now allowable, this completed form is considered to fulfill the response requirements of the last Office action. Applicant is not relieved from providing a separate record of the substance of the interview unless box 1 above is also checked.

Douglas J. McInty  
Examiner's Signature

Manual of Patent Examining Procedure, Section 713.04 Substance of Interview Must Be Made of Record

A complete written statement as to the substance of *any* face-to-face or telephone *interview* with regard to an application *must be made of record in the application*, whether or not an agreement with the examiner was reached at the interview.

§ 1.133 Interviews

.....

(b) In every instance where reconsideration is requested in view of an interview with an examiner, a complete written statement of the reasons presented at the interview as warranting favorable action must be *filed* by the applicant. An interview does not remove the necessity for response to Office actions as specified in § 1.111, 1.135. (35 U.S.C. 132)

§ 1.2 Business to be transacted in writing. All business with the Patent and Trademark Office should be transacted in writing. The personal attendance of applicants or their attorneys or agents at the Patent and Trademark Office is unnecessary. The action of the Patent and Trademark Office will be based exclusively on the written record in the Office. No attention will be paid to any alleged oral promise, stipulation, or understanding in relation to which there is disagreement or doubt.

The action of the Patent and Trademark Office cannot be based exclusively on the written record in the Office if that record is itself incomplete through the failure to record the substance of interviews.

It is the responsibility of the applicant or the attorney or agent to make the substance of an interview of record in the application file, unless the examiner indicates he or she will do so. It is the examiner's responsibility to see that such a record is made and to correct material inaccuracies which bear directly on the question of patentability.

Examiners must complete a two-sheet carbon interleaf interview Summary Form for each interview held after January 1, 1978 where a matter of substance has been discussed during the interview by checking the appropriate boxes and filling in the blanks in neat handwritten form using a ball point pen. Discussions regarding only procedural matters, directed solely to restriction requirements for which interview recordation is otherwise provided for in Section 812.01 of the Manual of Patent Examining Procedure, or pointing out typographical errors or unreadable script in Office actions or the like, are excluded from the interview recordation procedures below.

The interview Summary Form shall be given an appropriate paper number, placed in the right hand portion of the file, and listed on the "Contents" list on the file wrapper. The docket and serial register cards need not be updated to reflect interviews. In a personal interview, the duplicate copy of the Form is removed and given to the applicant (or attorney or agent) at the conclusion of the interview. In case of a telephonic interview, the copy is mailed to the applicant's correspondence address either with or prior to the next official communication. If additional correspondence from the examiner is not likely before an allowance or if other circumstances dictate, the Form should be mailed promptly after the telephonic interview rather than with the next official communication.

The Form provides for recordation of the following information:

- Serial Number of the application
- Name of applicant
- Name of examiner
- Date of interview
- Type of interview (personal or telephonic)
- Name of participant(s) (applicant, attorney or agent, etc.)
- An indication whether or not an exhibit was shown or a demonstration conducted
- An identification of the claims discussed
- An identification of the specific prior art discussed
- An indication whether an agreement was reached and if so, a description of the general nature of the agreement (may be by attachment of a copy of amendments or claims agreed as being allowable). (Agreements as to allowability are tentative and do not restrict further action by the examiner to the contrary.)
- The signature of the examiner who conducted the interview
- Names of other Patent and Trademark Office personnel present.

The Form also contains a statement reminding the applicant of his responsibility to record the substance of the interview.

It is desirable that the examiner orally remind the applicant of his obligation to record the substance of the interview in each case unless both applicant and examiner agree that the examiner will record same. Where the examiner agrees to record the substance of the interview, or when it is adequately recorded on the Form in an attachment to the form, the examiner should check a box at the Form informing the applicant that he need not supplement the Form by submitting a separate record of the interview.

It should be noted, however, that the interview Summary Form will not be considered and proper recordation of the interview unless it includes, or is supplemented by the applicant or the examiner to include, all of the applicable items required below concerning the substance of the interview:

A complete and proper recordation of the substance of any interview should include at least the following applicable items:

- 1) A brief description of the nature of any exhibit shown or any demonstration conducted.
- 2) an identification of the claims discussed.
- 3) an identification of specific prior art discussed.
- 4) an identification of the principal proposed amendments of a substantive nature discussed, unless these are already described on the Interview Summary Form completed by the examiner.
- 5) a brief identification of the general thrust of the principal arguments presented to the examiner. The identification of arguments need not be lengthy or elaborate. A verbatim or highly detailed description of the arguments not required. The identification of the arguments is sufficient if the general nature or thrust of the principal arguments made to the examiner can be understood in the context of the application office. Of course, the applicant may desire to emphasize and fully describe those arguments which he feels were or might be persuasive to the examiner.
- 6) a general indication of any other pertinent matters discussed, and
- 7) if appropriate, the general results or outcome of the interview unless already described in the interview Summary Form completed by the examiner.

Examiners are expected to carefully review the applicant's record of the substance of an interview. If the record is not complete or accurate, the examiner will give the applicant one month from the date of the notifying letter or the remainder of any period for response, whichever is longer, to complete the response and thereby avoid abandonment of the application (37 CFR 1.135(c)).

Examiner to Check for Accuracy

Applicant's summary of what took place at the interview should be carefully checked to determine the accuracy of any argument or statement attributed to the examiner during the interview. If there is an inaccuracy and it bears directly on the question of patentability, it should be pointed out in the next Office letter. If the claims are allowable for other reasons of record, the examiner should send a letter setting forth his or her version of the statement attributed to him. If the record is complete and accurate, the examiner should place the indication "interview record OK" on the paper recording the substance of the interview along with the date and the examiner's initials.



**UNITED STATES DEPARTMENT OF COMMERCE**  
**Patent and Trademark Office**  
Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

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|---------------|-------------|-----------------------|---------------------|
| 08/303,561    | 09/09/94    | BEDNORZ               | J Y0937074BY        |

11M1/0415  
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|                |              |
|----------------|--------------|
| MC GINEXAMINER |              |
|                |              |
| ART UNIT       | PAPER NUMBER |
| 1105           |              |

DATE MAILED:

04/15/96

*Due 7/15/96*

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents

## Office Action Summary

Application No.

08/303,561

Applicant(s)

Bednorz et al.

Examiner

Douglas J. McGinty

Group Art Unit

1105



☒ Responsive to communication(s) filed on April 11, 1996, January 3, 1996, and September 29, 1995

☐ This action is **FINAL**.

☐ Since this application is in condition for allowance except for formal matters, **prosecution as to the merits is closed** in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11; 453 O.G. 213.

A shortened statutory period for response to this action is set to expire 3 month(s), or thirty days, whichever is longer, from the mailing date of this communication. Failure to respond within the period for response will cause the application to become abandoned. (35 U.S.C. § 133). Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

### Disposition of Claims

☒ Claim(s) 24-26, 86-90, and 96-108 is/are pending in the application.

Of the above, claim(s) \_\_\_\_\_ is/are withdrawn from consideration.

☐ Claim(s) \_\_\_\_\_ is/are allowed.

☒ Claim(s) 24-26, 86-90, and 96-108 is/are rejected.

☐ Claim(s) \_\_\_\_\_ is/are objected to.

☐ Claims \_\_\_\_\_ are subject to restriction or election requirement.

### Application Papers

☐ See the attached Notice of Draftsperson's Patent Drawing Review, PTO-948.

☐ The drawing(s) filed on \_\_\_\_\_ is/are objected to by the Examiner.

☐ The proposed drawing correction, filed on \_\_\_\_\_ is ☐ approved ☐ disapproved.

☐ The specification is objected to by the Examiner.

☐ The oath or declaration is objected to by the Examiner.

### Priority under 35 U.S.C. § 119

☒ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☒ All ☐ Some\* ☐ None of the CERTIFIED copies of the priority documents have been

☐ received.

☒ received in Application No. (Series Code/Serial Number) 08/053,307.

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

\*Certified copies not received: \_\_\_\_\_

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

### Attachment(s)

☐ Notice of References Cited, PTO-892

☐ Information Disclosure Statement(s), PTO-1449, Paper No(s). \_\_\_\_\_

☐ Interview Summary, PTO-413

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

--- SEE OFFICE ACTION ON THE FOLLOWING PAGES ---

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**DETAILED ACTION**

1. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action. The rejections and objections, if any, from the previous Office Action have been withdrawn if not repeated in this Office Action.

2. It is requested that this Examiner be notified of all pending, related applications. See MPEP 2001.06(b). That notice need not be in a PTO form - 1449, however. See MPEP 901.03.

***Priority***

3. Acknowledgment is made of applicant's claim for priority under 35 U.S.C. § 119. The certified copy has been filed in parent application, Serial No. 08/053,307, filed on April 23, 1993 as paper no. 28.

a. However, a review of that certified copy, which is in English, indicates that it does not support the present assertion of priority. Support is not found in that certified copy for the invention as presently claimed. See MPEP 201.13 et seq. and 201.14 et seq.

b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The applicants quote some passages out of the priority document and argue that the present claims are fully based that document. Nevertheless, that priority document is not deemed to provide basis for the following limitations found in the present claims:

i. The limitations "a composition including a transition metal, a rare earth or rare earth-like element, an alkaline earth element, and oxygen", as found in claim 86 (lines 2-4). The certified priority document may provide basis for the

formula  $RE_2TM.O_4$  at p. 2, para. 4, but the claimed composition is deemed to be much broader than that formula.

ii. The limitation "non-stoichiometric amount of oxygen", as found in claim 86 (line 6). Basis may be seen for an oxygen deficit at p. 2, para. 4, but no such basis is seen for the more general limitation of "a nonstoichiometric amount of oxygen".

iii. The limitation "a composition exhibiting a superconductive state", as found in claim 88 (line 2), wherein the composition is a "(transition) metal oxide", as found in claims 24 (lines 1 and 2), 89 and 90. The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but "a composition", "metal oxide", or "transition metal oxide" is deemed to be much broader than the formula  $RE_2TM.O_4$ .

iv. The limitation "a copper-oxide compound", as recited in claim 96 (line 6). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but "a copper-oxide compound" is not deemed to be equivalent to a composition of the formula  $RE_2TM.O_4$ . Basis is not seen in the certified priority document for "a copper-oxide compound" with the breadth of the present claims.

v. The limitation to the effect that "the copper oxide compound includes (including) at least one rare-earth or rare-earth-like element and at least one alkaline-earth element", as recited in claim 97 (lines 3 and 4) and claim 103 (lines 6-8). The certified priority document may provide basis for compositions of the formula  $RE_2TM.O_4$ , as discussed above, but basis is not seen for the more general limitation of "a copper-oxide compound" with a rare-earth (like) element and an alkaline earth element.

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vi. The limitation to the effect that "the copper-oxide compound includes at least one element (oxygen) in a nonstoichiometric atomic proportion", as found in claim 101 (lines 2 and 3), 102 (lines 2 and 3), 107 (lines 2 and 3), and 108 (lines 2 and 3). Basis may be seen for an oxygen deficit as discussed above, but no such basis is seen for the more general limitation of "a nonstoichiometric atomic proportion".

vii. The limitation as to "the effectively-zero-bulk-resistivity intercept temperature  $T_{p=0}$ ", as found in claim 103 (lines 13, 16, and 17). The critical temperature,  $T_c$ , is discussed throughout that certified priority document, but not  $T_{p=0}$ .

*Claim Rejections - 35 USC § 112*

4. The specification is objected to under 35 U.S.C. § 112, *first paragraph*, as failing to provide an enabling disclosure commensurate with the scope of the claims.

a. The present specification is deemed to be enabled only for compositions comprising  $Ba_xLa_{5-x}Cu_3O_y$ . The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases.<sup>1</sup> Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112.<sup>2</sup> Merely reciting a desired result does not

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<sup>1</sup>See In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218. See also, In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977) (J. Rich).

<sup>2</sup>See In re Cook, 169 USPQ 298, 302; and Cosden Oil v. American Hoechst, 214 USPQ 244, 262.

overcome this failure.<sup>3</sup> In particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?

b. It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion".<sup>4</sup>

c. Claims 24-26, 86-90, and 96-108 are rejected under 35 U.S.C. § 112, *first paragraph*, for the reasons set forth in the objection to the specification.

d. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The additional caselaw and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is deemed to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed.

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<sup>3</sup>See In re Corkill, 226 USPQ 105, 1009.

<sup>4</sup>See Brenner v. Manson, 383 US 519, 148 USPQ 689.



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ii. The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K.

iii. Construed in light of that issue, the invention is not deemed to have been fully enabled by the disclosure to the extent presently claimed.

(1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

(a) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the **scope** presently claimed. The claims include formulae which are much broader than the RE-TM-O formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

(b) The present specification actually shows that known forms of "a transition metal oxide", "a composition", and "a copper-oxide compound" do **not** show the onset of superconductivity at above 26°K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K." Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, non-conducting CuO phase" at p. 14, line 18.

(c) Accordingly, the present disclosure is not deemed to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88, or the "copper-oxide compound" of claim 96.

(2) The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed.

(a) With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-O", per p. 8, line 11) shows "no superconductivity".

(b) With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that **all** of the claims in this application require the critical temperature ( $T_c$ ) to be "in excess of  $26^\circ\text{K}$ " or "greater than  $26^\circ\text{K}$ ".

(c) Consequently, the present disclosure is not deemed to adequately enable the full scope of the present claims. Independent claims 86 and 103 may require the presence of rare earth, alkaline earth, and transition metals, but the aforementioned examples show that superconductivity is still very unpredictable. Those claims cannot be deemed to be fully enabled.

iv. The applicants also have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct  $> 26^\circ\text{K}$ . Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above  $26^\circ\text{K}$ , such a person of skill in the art, using the techniques

described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ...without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art." All three affiants apparently are the employees of the assignee of the present application.

(1) Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.<sup>5</sup>

(2) Those affidavits do not overcome the non-enablement rejection. The present specification discloses *on its face* that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at  $> 26^{\circ}\text{K}$ .

(3) Those affidavits are not deemed to shed light on the state of the art and enablement *at the time* the invention was made. One may know *now* of a material that superconducts at more than  $26^{\circ}\text{K}$ , but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

(4) It is fully understood that the applicants are the pioneers in high temperature metal oxide

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<sup>5</sup>See In re Lindner, 173 USPQ 356, 358 (CCPA 1972).

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superconductivity. The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims.

5. Claims 86-87 and 96-108 are rejected under 35 U.S.C. § 112, *second paragraph*, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

a. The terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing. The question arises: What is meant by these terms?

b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The terms "layer-type" and "perovskite-like" are unclear because the "type" or "like" terms are deemed to be indefinite. Terms such as "like", "similar", and "type" are indefinite.<sup>6</sup> It is suggested that "layer-type perovskite-like crystal structure" be changed -- a substantially layered perovskite crystal structure --.

ii. The applicants respond that "(a) person of skill in the art would understand (rare earth-like) to mean that a location occupied by a rare earth element can also be occupied by another element which would have chemical properties similar enough to the rare earth elements such that it would fit in to the latter (sic - lattice?) site occupied by the rare earth element." That response does not alleviate the problem, however.

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<sup>6</sup>See Ex parte Remark, 15 USPQ 2d 1498, 1500 (BPAI 1990); Ex parte Kristensen, 10 USPQ 2d 1701, 1703 (BPAI 1989); Ex parte Attig, 7 USPQ 2d 1092, 1093 (BPAI 1988); and Ex parte Copenhaver, 109 USPQ 118 (POBA 1955).

Other elements may "fit" into the lattice but they may not necessarily be "rare-earth-like". It is suggested that the same language be changed to -- Group III B --, per p. 7, line 11, of the present specification.

*Claim Rejections - 35 USC § 102*

6. Claims 24-26, 86-90, and 96-108 are rejected under 35 U.S.C. § 102(a) as being anticipated by Asahi Shinbum, International Satellite Edition (London), November 11, 1986 (hereinafter, "the Asahi Shinbum article").

a. As discussed in paper no. 20 of the ancestral application, 07/053,307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later than around December 13, 1986, the date samples were tested in the US to show superconductivity. See MPEP 715 et seq. The Asahi Shinbum article was published on November 28, 1986.

b. The reference confirms superconductivity in an oxide compound of La and Cu with Ba having a structure of the so-called perovskite structure. Although the reference fails to teach use of the testing of zero resistance for confirming superconductivity, it inherently must have been used because it is one of two methods used for testing for superconductivity (the other being diamagnetism). Accordingly, the burden of proof is upon the applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference.<sup>7</sup>

c. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996,

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<sup>7</sup>See In re Brown, 173 USPQ 685, 688; In re Best, 195 USPQ 430; and In re Marosi, 218 USPQ 289, 293.

paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive.

i. The applicants argue that the Sung II Park Affidavit of March 30, 1988 states at para. 4 that measurements were taken of a superconductive sample on or before November 9, 1986, to the best of the affiant's recollection, or no later than November 15, 1986. The documentary evidence is not deemed to support that argument, however. See MPEP 715.07.

(1) Plots of those measurements are missing. See the Chang C. Tsuei Affidavit of March 30, 1988, para. 6. A hand-drawn diagram with the indication of vacuum pumping on November 9, 1988 also is not deemed to show that the measurements were taken.

(2) Moreover, the other evidence in the record appears to show that high temperature superconductivity was not attained in this country as of November 9 or 15, 1986. The March 30, 1986 Declaration of Richard L. Greene includes a series of cablegrams sent by Dr. Greene to the applicants in Zurich, Switzerland as Exhibit B. On both November 11, 1986 and November 14, 1986, Dr. Greene reports that no indication of superconductivity has been seen in his specific heat measurements for temperatures of 4-35°K. Exhibit C has pages dated December 1, 1986 on, and Exhibit D, which actually has plots of resistance vs. temperature, has an earliest date of December 3, 1996.

ii. The applicants assert that the Asahi Shinbum article reports a third party's confirmation of their original discovery. That assertion appears to be correct, but the article still is deemed to be prior art under 35 USC 102(a).

(1) It should be noted again, however, that the applicants' discovery was not originally made in this country and that they cannot show an earlier date than December 1986 for their invention in this country. The Asahi Shinbum article was published on November 28, 1986.

(2) The applicants cite four decisions<sup>8</sup> which do not directly apply to the present facts.

(a) The In re Katz<sup>9</sup> decision held that an applicant may overcome an article as 35 USC 102(a) prior art by showing that the applicant was a co-author and that the other co-authors were under the direction and control of the applicant. Here, however, the applicants were neither co-authors in the Asahi Shinbum article nor did they exercise direction and control over the work reported in that article.

(b) The Andrews v. Hovey<sup>10</sup> decision involved a grace period which is now codified in 35 USC 102(b). The present case involves a printed publication as prior art under 35 USC 102(a).

(c) The Ex parte Powell and Davies<sup>11</sup> decision held that an applicant's own foreign patent which issued within the grace period cannot be used against him or her, and the Ex parte Lemieux<sup>12</sup> decision applied that reasoning to an applicant's own article published in another country. Again, the present applicants had no part in the writing of the Asahi Shinbum article.

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<sup>8</sup>One decision is cited in the January 4, 1996 Supplementary Response, paper no. 51: In re Katz, 215 USPQ 14 (CCPA 1982). Three decisions are cited in the April 11, 1996 Supplementary Response, paper no. 53: Andrews v. Hovey, 123 US 267 (1887); Ex parte Lemieux, 115 USPQ 148 (POBA 1957); and Ex parte Powell and Davies, 37 USPQ 285 (POBA 1938).

<sup>9</sup>See In re Katz, *supra*, 215 USPQ at 17, 18. See also, MPEP 716.10.

<sup>10</sup>See Andrews v. Hovey, *supra*.

<sup>11</sup>See Ex parte Powell and Davies, *supra*, 37 USPQ at 285, 286.

<sup>12</sup>See Ex parte Lemieux, *supra*, 115 USPQ at 149. See also, MPEP 715.01(c).

(3) The present facts may raise a novel issue of law.<sup>13</sup> The applicants were the first to develop the presently claimed invention, but the earliest date they can show for that invention in this country is December of 1986.<sup>14</sup> The Asahi Shinbum article was published in November of 1986 and describes the development of superconductivity with an oxide of La, Ba, and Cu having a perovskite structure by a third party, but that article apparently indicates that the third party was confirming the discovery of the present applicants. Notwithstanding the possible uniqueness of the present facts, however, the Asahi Shinbum article still is deemed to be prior art under 35 USC 102(a), which the applicants have not been able to overcome with a showing of an earlier date in this country or a showing of their direction and control over the work done by that third party.

*Claim Rejections - 35 USC § 103*

**7. Claims 24-26, 86-90, and 96-108 are rejected under 35 U.S.C. § 103 as being unpatentable over the Asahi Shinbum article.**

a. The reference is relied upon as set forth in the previous rejection. This reference may differ from the present claims in that it may fail to disclose the presently claimed method of "causing an electric current to flow in the superconductor element". It was notoriously well-known in the art of superconductors that a method of utilizing superconductive

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<sup>13</sup>The applicants did not cite In re Mathews, 161 USPQ 276, 277-279 (CCPA 1969), which held that an applicant may overcome a patent as prior art under 35 USC 102(e) with evidence that the applicant provided the knowledge for the disclosure in that patent. By contrast, the present facts involve prior art under 35 USC 102(a) with a publication date **before** the invention was in this country.

<sup>14</sup>The applicants' proposed priority date for the EPO application is January 23, 1987, which is after the December 1986 dates show by the Richard L. Greene Affidavit.



materials was to cause an electric current to flow in the material while it is cooled below its transition temperature. See MPEP 706.02(a). Accordingly, it would have been well within the purview of one of ordinary skill to use the present claimed method with the materials disclosed by the reference. One would have been motivated to cool the material of the reference to below the transition temperature and cause electric current to flow in the material to provide electricity without resistance. Accordingly, the present claims are unpatentable in view of the prior art of record.

b. Applicants' arguments filed April 11, 1996, January 3, 1996, and September 29, 1995, paper nos. 53, 50, and 51, as well as the Affidavits filed September 29, 1995 and January 3, 1996, paper nos. 49 and 52, have been fully considered but they are not deemed to be persuasive. The Asahi Shinbum article is deemed to be prior art under 35 USC 102(a) for the reasons discussed above.

***Possibly Allowable Subject Matter***

8. It is noted that the applicants were awarded the Nobel Prize for their work in this area. The record is not deemed to indicate, however, that the Asahi Shinbum article was predicated by the applicants' earlier conception and/or reduction to practice *in this country*. The presently claimed invention also is non-enabling and indefinite for the reasons set forth above.

9. To possibly overcome the above rejections, the following amendments are suggested:

a. 109 (New). A method comprising the steps of:

forming a composition of the formula  $Ba_xLa_{3-x}Cu_3O_y$ , wherein x is from about 0.75 to about 1 and y is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which

exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical current through said composition while said metal oxide phase is in said superconducting state.

b. Cancel claims 24-26, 86-90, and 96-108.

10. The following is an Examiner's statement of reasons for the indication of possibly allowable subject matter:

a. The Asahi Shinbum article teaches in general that perovskite-like compounds of La, Cu, and Ba have a  $T_c$  of 30°K, but that article apparently does not teach the particular formula in the amendment suggested above. The examples in the present specification are deemed to show criticality for that formula in that suggested amendment.

b. Support for the proposed amendment is found at p. 20, line 1, through p. 25, line 5, and in Figure 3.

Serial Number: 08/303,561

-16-

Art Unit: 1105

c. This indication of possibly allowable subject matter is subject to further consideration and review.

*Conclusion*


11. Any amendment in response to this Office Action must NOT include any new matter. See MPEP 608.04 and 706.03(o).

12. The applicant or applicants is or are reminded that any evidence to be presented in accordance with 37 CFR 1.131 or 1.132 should be submitted before final rejection in order to be considered timely.

13. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Douglas J. McGinty, whose telephone number is (703) 308-3805. The examiner normally can be reached on Monday through Friday from 8:30 A.M. to 5:00 P.M., Eastern time. If reasonable attempts to reach the examiner by telephone are unsuccessful, however, the examiner's supervisor, Mr. Paul Lieberman, can be reached at (703) 308-2523. Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

14. The fax number for this Group is (703) 305-3600.

April 12, 1996  
303561.2

  
Douglas J. McGinty  
Primary Examiner  
Group 1100

\*\* TX CONFIRMATION REPORT \*\*

AS OF APR 11 '96 15:36 PAGE.01

IBM IPLAW-RES

|    | DATE | TIME  | TO/FROM      | MODE  | MIN/SEC | PGS | CMD# | STATUS |
|----|------|-------|--------------|-------|---------|-----|------|--------|
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Thomas J. Watson Research Center  
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Date: 4-11-96

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Contact #: \_\_\_\_\_

From:

Name: Daniel P. Morris

Phone: \_\_\_\_\_

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. Bednorz et al.

Date: April 11, 1996

Serial No.: 08/303,561

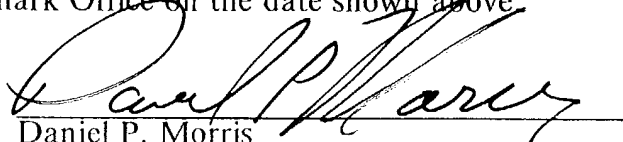
Group Art Unit: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

I hereby certify that this paper is being facsimile transmitted under Rule 37 CFR §  
1.161(d) to the U.S. Patent and Trademark Office on the date shown above.

  
Daniel P. Morris  
Reg. No. 32,053

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

SUPPLEMENTARY RESPONSE

Sir:

In response to the Office Action dated March 19, 1995, please consider the following:

REMARKS

These remarks are in addition to those of the previously submitted response.

Claims 24-26, 86-90 and 96-108 have been rejected under 35 USC § 102(a) as being  
anticipated by the Asahi Shinbum article and under 35 USC § 103 in view of the Asahi

Shinbum article. In addition to Applicants' remarks in regard to this rejection in Applicant's prior response, please consider the following:

The date of the Asahi Shinbum article is November 28, 1986. As stated in Applicants' specification at page 6, lines 7-10:

The basis for our invention has been described by us in the following previously published article: J.G. Bednorz and K.A. Mueller, Zeitschrift for Physik B - Condensed Matter, 64, pp. 189-193, Sept. (1986).

The Examiner is using Asahi Shinbum as a reference under 35 USC § 102(a). Applicants respectfully disagree since to do so does not permit Applicants the one year period provided under 35 USC § 102(b) to file a U.S. application after their own publication which permitted Applicants to file the present application up to September 1987. The date of the Asahi Shinbum article is after the date of Applicants' publication.

In regard to the two-year grace period under a prior statute, the U.S. Supreme Court in *Andrews v. Hovey*, 123 US 267 (1887) states that:

"The evident purpose of the section was to fix a period of limitation which should be certain, and require only a calculation of time, and should not depend upon the uncertain question of whether the Applicant had consented to or allowed the sale or use. Its object was to require the inventor to see to it that he filed his application within two years from the completion of his invention, so as to cut off

all question of the defeat of his patent by a use or sale of it by others more than two years prior to his application, and thus leave open only the question of priority of invention. The evident intention of congress was to take away the right (which existed under the act of 1836) to obtain a patent after an invention had for a long period of time been in public use, without the consent or allowance of the inventor; it limited that period to two years, whether the inventor had or had not consented to or allowed the public use."

From this quote from *Andrews v. Hovey*, it is evident that the use or sale by others prior to filing a patent application by the inventor does not cut off the inventors right to obtain a patent so long as the inventor files the application within the statutory period which was 2 years at the time of the *Andrews v. Hovey* decision and is now 1 year under 35 USC 102(b).

The Patent Office Board of Appeals in *Ex parte Powell and Davies*, 37 USPQ 285 states in regard to the publication of Applicants foreign patent application before the filing of a U.S. application on October 5, 1936 on an invention described in the foreign patent application that:

The Examiner has also rejected the claims on the printed specification of Applicants' own British application which appears from this record to have been published on August 27, 1936. We know of no authority for such a rejection. Neither section 3886 nor section 4887 R.S. warrants the rejection. Obviously, the publication could not have a date



prior to Applicants' invention. There is no statute that requires an Applicant to make his invention in this country.

Therefore, Applicants of the present invention can rely on their publication in Zeitschrift for Physik as evidence of their invention.

The Patent Office Board of Appeals in Ex parte Powell and Davies, 37 USPQ 285, 286 further states:

The Commissioner indicates in Ex parte Grosselin that the Examiner should consider whether the German patent was derived from Applicant and was in effect nothing more than a printed publication of Grosselin's invention.

The Asahi Shinbum article states in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

The "scientists in Switzerland" are the inventors of the above-identified application. The Asahi Shinbum article only reports the work of Applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of Applicants' "own invention" and clearly

in the words of the Board in Ex parte Powell and Davies, "was derived from [Applicants] and [is] in effect nothing more than a printed publication of [Applicants'] own invention and cannot be used as a reference.

The Patent Office Board of Appeals in Ex parte Lemieux 148, 140 states that:

Finally, we believe that our holding is consistent with decisions in interference practice wherein, even though in the usual case a party may not establish a priority date of invention by reference to activity in a foreign country, yet in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad. ... By analogy, in the present case appellant has demonstrated that he is the single original inventor, there being no adverse party.

Following this decision it is clear from the Asahi Shinbum article that Applicants are the "single original inventor" and that the Asahi Shinbum article is "derived" from Applicants and that Professor Tanaka's work reported in the Asahi Shinbum article is "derived" from Applicants.

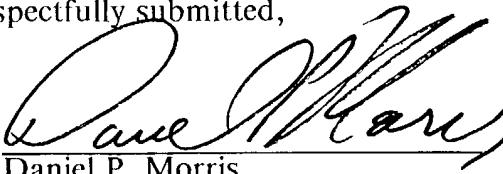
Therefore, the Examiner is respectfully requested to withdraw the rejection of claims 24-26, 86-90 and 96-108 under 35 USC § 102(a) as anticipated by Asahi Shinbum and under 35 USC § 103 as obvious over Asahi Shinbum.

Attached are copies of the following decisions:

Ex parte Powell and Davies 37 USPQ 285

Ex parte Lemieux 115 USPQ 148

Respectfully submitted,

By:   
Daniel P. Morris  
Reg. No. 32,053

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598  
(914) 945-3217

## Patent Office Board of Appeals

Ex parte LEMIEUX

Patent issued Oct. 8, 1957

Opinion dated July 31, 1957

## PATENTS

1. Interference—Reduction to practice—  
In general (§ 41.751)

Patentability—Anticipation—In general (§ 51.201)

Patentability — Anticipation — Publications—In general (§ 51.2271)

Act of August 8, 1946 (35 U.S.C. 104) was enacted to overrule *Electric v. Shimadzu*, 307 U.S. 5, 41 USPQ 155, and preclude applicant or patentee from relying upon foreign activity to establish date of invention; it had no effect on *Ex parte Powell*, 37 USPQ 285; hence, inventor's foreign publication within year prior to filing United States application does not bar him from obtaining patent.

## 2. Affidavits — Anticipating references (§ 12.3)

Rule 131 does not apply where publication is publication of applicant's own invention; domestic inventors are not distinguished from foreign inventors; all that is required is that identity of applicant inventor and publication author be established.

## 3. Interference — Originality of invention—In general (§ 41.551)

Interference—Reduction to practice—  
In general (§ 41.751)

Even though in usual case interference party may not establish priority date of invention by reference to activity in foreign country, in originality case, where party is seeking to prove that opponent derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad.

Particular patents—Ustilic Acids

2,809,205, Lemieux, Production of Ustilic Acids, claims 1 to 4 and 6 of application allowed.

Appeal from Division 63.

Application for patent of Raymond U. Lemieux, Serial No. 281,451, filed Apr. 9, 1952. From decision rejecting claims 1 to 4 and 6, applicant appeals. Reversed. *PIERCE, SCHEFFLER & PARKER*, Washington, D.C., and *ALEX E. MACRAE* for applicant.

Before *DUNCOMBE*, Examiner in Chief, and *MAGIL* and *BREWRINK*, Acting Examiners in Chief.

*MAGIL*, Acting Examiner in Chief.

This is an appeal from the final rejection of claims 1 through 4 and 6. Claims 5 and 7, the remaining claims in the case, have been withdrawn from further consideration in accordance with Rule 142(b) and are not before us.

Since the issue involved in this case is purely legal in nature, there is no reason for reproducing an illustrative claim.

The reference relied upon is:

Lemieux, Canadian Journal of Chemistry, Vol. 29, (May 1951), pages 415-425.

We need not refer to the subject matter of the claims because, as previously indicated, the appeal involves only a legal point. The following facts are not in dispute:

1. The appellant is the author of the cited publication.

2. The subject matter of the appealed claims is adequately disclosed in the cited publication.

3. The cited article was published prior to appellant's filing date in this country, but not more than one year prior thereto.

4. Appellant does not rely upon any earlier filing date to antedate the publication, nor does he assert that he completed the invention in this country prior to the date of the publication.

The examiner holds that appellant is barred from obtaining a patent by the provision of 35 U.S.C. 102(a) and that he cannot avoid this bar because of the restriction of 35 U.S.C. 104 and the words "in this country" in Rule 131.

Appellant contends that he filed his application within the one year period specified in 35 U.S.C. 102(b) and that Rule 131 is inapplicable. Appellant relies upon the case of *Ex parte Powell* and *Davies*, 489 O.G. 231, 1938 C.D. 15, 37 USPQ 285; he also refers to the International Convention for the Protection of Industrial Property and to the effect of the examiner's rejection on Canadian inventors.

We have carefully considered the examiner's rejection and the appellant's arguments and have studied the pertinent cases on this subject. On its face, and disregarding subsequent statutory changes, the *Powell* and *Davies* case appears to be most apposite. The examiner recognizes that the cited decision is relevant, but holds that it is no longer controlling because of the Act of August 8, 1946, which resulted in the enactment of the statute presently corresponding to 35 U.S.C. 104.

[1] We have U.S.C. 104 and by the case of *Shimadzu et al.*, 675, 83 Law. 504 O.G. 4, 41 in an infringement not precluded invention by abroad. We the *Shimadzu* country" in ol to present Rule the case of In 810, 1942 C.D. F.2d 169, 52 U the *Shimadzu* anomalous situation in inte another rule a ings. In order the Act of Au and, as is evi No. 1502, June 2nd Session, at January 28, Session, the p effect, to overr tation of the S clude an appl relying upon f a date of inven case is referre Senate and the

With the fo be said that t the Act of A to overrule the it had no eff Davies decision Powell and I affected, we s trolling in the reversal of the note that the was cited by t In re Saurer, 405, 529 O.G. 8 78, but the Co applicable on failed to estal person named also state tha Ex parte Gro C.D. 248, cited decision, as v Ex parte Gro C.D. 163, to b

Aside from 104, there is section is not case. Appella lish a date of argued that h publication an the examiner. of invention

in the final rejection 4 and 6. Claims 1 and 2 in the case, from further consideration with Rule 142(b)

involved in this case, there is no illustrative

upon is:

Journal of Chemical Physics, 1951, pages 415-

the subject matter as previously involves only a legal facts are not in

the author of

matter of the apparently disclosed

was published during date in this more than one year

not rely upon any to antedate the he assert that invention in this date of the pub-

that appellant is a patent by the 102(a) and that because of the 104 and the in Rule 131.

that he filed his one year period 102(b) and that

Appellant re-Ex parte Powell 1, 1938 C.D. 15, refers to the for the Property and to er's rejection on

considered the ex- the appellant's studied the pertinent. On its face, quent statutory Davies case ap- The examiner decision is relevant no longer correct of August 8, the enactment of corresponding to

[1] We have traced the history of 35 U.S.C. 104 and find that it was prompted by the case of *Electric Storage Co. v. Shimadzu et al.*, 307 U.S. 5, 59 Sup.Ct. 675, 83 Law. Ed. 1071, 1939 C.D. 870, 504 O.G. 4, 41 USPQ 155, which held that in an infringement action the patentee is not precluded from proving his date of invention by reference to his activity abroad. We note that, on the basis of the Shimadzu decision, the words "in this country" in old Rule 75, corresponding to present Rule 131, were held invalid in the case of *In re McFarlane*, 29 C.C.P.A. 810, 1942 C.D. 254, 540 O.G. 237, 125 F.2d 169, 52 USPQ 335. The decision in the Shimadzu et al. case created an anomalous situation, with one rule applying in interference proceedings and another rule applying in other proceedings. In order to remedy this situation, the Act of August 8, 1946 was enacted and, as is evident from Senate Report No. 1502, June 14, 1946, 79th Congress, 2nd Session, and House Report No. 1498, January 28, 1946, 79th Congress, 2nd Session, the purpose of the law was, in effect, to overrule the statutory interpretation of the Shimadzu decision and preclude an applicant or a patentee from relying upon foreign activity to establish a date of invention. The Shimadzu et al. case is referred to by name in both the Senate and the House Reports.

With the foregoing analysis, it may be said that the purpose and effect of the Act of August 8, 1946 was solely to overrule the Shimadzu et al. case and it had no effect upon the Powell and Davies decision cited by appellant. The Powell and Davies decision being unaffected, we should hold that it is controlling in the present case and dictates reversal of the examiner's decision. We note that the Powell and Davies case was cited by the appellant in the case of *In re Saurer*, 28 C.C.P.A. 1021, 1941 C.D. 405, 529 O.G. 802, 118 F.2d 719, 49 USPQ 78, but the Court found the decision inapplicable only because the appellant failed to establish his identity with the person named in the reference. We may also state that we consider the case of *Ex parte Grosselin*, 97 O.G. 2977, 1901 C.D. 248, cited in the Powell and Davies decision, as well as the earlier case of *Ex parte Grosselin*, 84 O.G. 1284, 1898 C.D. 163, to be pertinent.

Aside from the history of 35 U.S.C. 104, there is another reason why this section is not applicable to the present case. Appellant is not seeking to "establish a date of invention" but has merely argued that he is the author of the cited publication and this is not disputed by the examiner. There being no evidence of invention by anyone else prior to

appellant's filing date, the date of appellant's invention is immaterial. In the present case, we are not concerned with appellant's "date of invention" vis-a-vis the publication of another, an interferent, or other adverse party.

[2] Insofar as the requirements of Rule 131 are concerned, we need do nothing more than refer to and state our agreement with the holdings in the first Grosselin decision (84 O.G. 1284, 1898 C.D. 163) and in the Powell and Davies case concerning old Rule 75, corresponding to present Rule 131. In the former decision it was held that "this rule presupposes that the printed publication is the publication by some one other than the applicant whose application is rejected by some one who asserts inventorship therein either in himself or some other person than the applicant." In the later case it was held that the rule is not "intended to apply to a case where the publication appears without question to be a publication of the applicant's own invention."

We also take cognizance of several decisions (*Ex parte Ensign*, 2 USPQ 214; *Ex parte Layne*, 63 USPQ 17; *Ex parte Hirschler*, 110 USPQ 384) which have held that, apparently in the case of a domestic inventor, a publication dated less than a year prior to the filing date of an application is not an effective bar if the applicant makes a satisfactory showing that the publication is his own invention or that he is, in effect, the author of the publication. In none of these cases is there any indication that the applicant made the usual showing under Rule 131, that is, reduction to practice prior to the date of the publication or conception prior to the date of the publication coupled with the necessary diligence. We find no reason for distinguishing between a domestic inventor and a foreign inventor in situations of this type and all that is required is that the identity of the application inventor and the publication author be established. There is no dispute on this point in the present case.

[3] Finally, we believe that our holding is consistent with decisions in interference practice wherein, even though in the usual case a party may not establish a priority date of invention by reference to activity in a foreign country, yet in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad. *Shiels v. Lawrence and Kennedy*, 81 O.G. 2085, 1897 C.D. 184; *Stiff v. Galbraith*, 108 O.G. 290, 1904 C.D. 10. By analogy, in the present case appellant has demonstrated

that he is the single original inventor, there being no adverse party.

In accordance with the foregoing reasoning, we conclude that the examiner's rejection cannot be sustained. We do not consider it necessary to discuss appellant's arguments concerning the International Convention for the Protection of Industrial Property or the effect of the examiner's rejection on Canadian inventors.

The decision of the examiner is reversed.

### Patent Office Board of Appeals

Ex parte BERGMANN

Patent issued Oct. 8, 1957

Opinion dated Jan. 22, 1957

### PATENTS

#### 1. Patentability — Change — Material (§ 51.257)

Claims are allowed where applicant did not merely indulge in routine experimentation with material having properties which would be expected to produce results desired, but utilized to advantage a material whose properties appeared to be unfavorable.

Particular patents—Sound Recording 2,809,237, Bergmann, Magnetic Sound Recording Head, claims 1 and 3 to 7 of application allowed.

Appeal from Division 16.

Application for patent of Friedrich Bergmann, Serial No. 209,250, filed Feb. 3, 1951. From decision rejecting claims 1 and 3 to 7, applicant appeals. Reversed. MARZALL, JOHNSTON, COOK & ROOR, Chicago, Ill., for applicant.

Before TAYLOR and KREEK, Examiners in Chief, and NILSON, Acting Examiner in Chief.

KREEK, Examiner in Chief.

This is an appeal from the final rejection of claims 1 and 3 to 7 inclusive. No claims have been allowed.

Claim 1 is illustrative:

1. Magnetic sound recording head having a core consisting exclusively of magnetic ferrite.

The references relied on are:

|            |           |               |
|------------|-----------|---------------|
| Burns      | 2,536,260 | Jan. 2, 1951  |
| Buhrendorf | 2,592,652 | Apr. 15, 1952 |

As is apparent from the illustrative claim, the subject matter here on appeal relates to a recording head for a magnetic sound recorder in which the core consists exclusively of magnetic ferrite. Numerous advantages are claimed for this construction among which are reduction of wear on the core as a result of the magnetic record medium passing thereover, as compared to the wear of conventional iron cores under similar circumstances; and reduction in electrical losses especially at high frequencies.

Claims 1 and 3 to 7 were rejected as being unpatentable over Buhrendorf or Burns in view of the general knowledge of the art, the examiner's position being "The routine examination of any known substance for a particular use is expected where the known basic requirements of the use are compatible with some characteristics of the substance." It is his opinion "that the mere knowledge that 'ferrites' are magnetic is enough to warrant investigation by workers in magnetic recording. The knowledge of their high frequency losses and avowed utility in electro-acoustic devices practically demands investigation."

Appellant contends that the references relied on do not suggest making cores exclusively of ferrite, and that the known permeability, saturation and abrasive characteristics of ferrite would point away from its use in sound recording heads rather than suggest it. He asserts that recording heads heretofore used are made with cores of highly permeable material to secure proper operation, but that satisfactory operation is secured with ferrite cores even though the permeability thereof is considerably less than the magnetic materials previously used. He asserts that the smaller magnetic saturation of ferrite as compared with metallic magnetic material would tend to indicate its unsuitability in erasing heads where high magnetic saturation is required. He further asserts that the fact ferrite would not abrade the surface of the sound band was surprising since sintered ferrite behaves somewhat like sintered porcelain. This characteristic which would have been expected to be detrimental is alleged to provide a great advantage resulting in heads having a life at least ten times longer than that of metal heads heretofore used. Appellant has made of record a publication by Rolf Cruel in Technische Hausmitteilungen des Nordwestdeutschen Rundfunks which compares magnetic heads made with ferrite with previously used laminated, high permeability iron alloy, which publication demonstrates important technical advantages possessed by ferrite over previously used magnetic materials. These are summarized as greater hard-

ness resulting in gr assistance to wear so used for much long without adjustment, high frequency and for erasing.

We have carefully in view of appellant various publications show the suitability material for recording of which we are of the rejection cannot be sustained.

The patent to Buhrendorf for magnetic recording heads using magnetic materials such as ferrite having high permeability. Claims are made extreme reduction of an inch thick reduce eddy current value as is feasible capability to work with ferrite. Obviously Buhrendorf anticipatory value, but the problems confronting this field as of the time Buhrendorf application.

Burns shows a magnetic recording head for magnetic record utilizing a central yoke either side of which are iron pole pieces 11 and contact the surface of the tape used in the recorder. The ferrite forms a part of the circuit, the frequency of the signal is a result of the variation in flow through the ferrite. It is noted, however, that the ferrite pieces are necessary to prevent the ferrite tape from being frequency currents flow through the ferrite core. There is no suggestion in Burns that the ferrite core may be made of ferrite. [1] The examiner asserts that low permeability ferrite is a factor as he states "such a material would be undesirable permeable material." It is the teachings of the prior art that the point away from the material having low permeability as ferrite as the sole material for a sound recording head. Withstanding this, the prior art clearly shows that in the use of ferrite, the permeability of ferrite, the magnetic properties are not as satisfactory as those of a magnetic recording head. It is significantly, however, that the use of ferrite have a resistance to abrasion and operate up to ten times longer than conventional metallic iron without adjustment. This is an important factor in recording heads.

## Patent Office Board of Appeals

Ex parte POWELL and DAVIES

Appl. No. 23985

Patent issued Apr. 5, 1938—Opinion dated Mar. 1, 1938

## Patents—Patentability—Anticipation—Foreign patents; Affidavits—Anticipating references (Rule 75)—

Applicants' own British patent has not been sealed, so there is no reason for registry under Rule 29; the British application was published in Aug., 1936, but there is no authority for basing on it rejection of United States application filed less than two years after such publication; Rule 75 was intended to provide ex parte means by which applicant can overcome rejection based on publication not more than two years prior to his invention but does not apply to case where publication appears without question to be publication of applicant's own invention.

## Patents—Electrodeposition of Silver—

2113517, Powell and Davies, Electrodeposition of Silver, claims 1, 2, 4 to 7, 10 and 11 of application allowed.

Patent No. 2113517 for electrodeposition of silver issued on application filed Oct. 5, 1936.

Appeal from Division 56.

HOWSON & HOWSON for applicants.

Before VAN ARSDALE, Assistant Commissioner, and REDROW and PORTER, Examiners in Chief.

PORTER, Examiner in Chief.—This is an appeal from the final rejection of claims 1, 2, 4 to 7, 10 and 11.

Claim 7 is illustrative.

7. A plating bath comprising a potassium argento-cyanide, an excess of free potassium cyanide, carbon disulphide and Turkey red oil.

The references relied upon are as follows:

Schlottter (British) 443,428, Feb. 27, 1936.

Powell et al (British) 450,979, Aug. 27, 1936.

Blum & Hogaboom, Principles of Electroplating (2nd Ed.) 1930, pages 350, 355 to 357.

It appears from Blum and Hogaboom that the silver plating solution of the claims is old except for the addition of alkali metal soaps or their equivalents. Blum et al describe an excess of free alkali metal cyanide but the British patent indicates that this excess should be very large and describes the use of Turkey red oil to which applicants refer at the bottom of page 3 of their specification. The British patent does not suggest the use of carbon bisulphide but rather suggests a substitute therefor. Blum et al does not suggest the use of soap. It is the combined use of carbon bisulphide and soap in the silver plating which applicants describe as their invention. The gist of the examiner's position with respect to the references referred

to appears to be that there is no invention in the combined use of the carbon bisulphide and soap in the silver plating bath. The trouble with this position is that it is not warranted by the record which does not show carbon bisulphide combined with a dispersing agent of the nature of the one employed by applicants.

The examiner has also rejected the claims on the printed specification of applicants' own British application which appears from this record to have been published on August 27, 1936. We know of no authority for such a rejection. Neither section 4886 nor section 4887 R. S. warrants the rejection. Obviously, the publication could not have a date prior to applicants' invention. There is no statute that requires an applicant to make his invention in this country.

It does not appear that the British patent has been sealed which sealing would be necessary in the case of a British patent in a rejection under Rule 29 and it appears from the decision of the Supervisory Examiner (Paper No. 7) that the examiner's real position is not that applicants are barred by the provisions of Rule 29 as appears from his statement, but that applicants have failed to overcome their own publication by affidavits filed under Rule 75.

Applicants filed a petition to the Commissioner asking that the examiner be instructed to withdraw the citation of their own British specification as a reference against the claims. This the Commissioner refused to do indicating that an adverse decision on the point by him might act to preclude a favorable decision by the Board of Appeals.

The examiner holds the affidavits insufficient as the nature of the contents of the notes referred to in the affidavit of Coussmaker does not appear and there is no such showing as to facts as is

necessary in affidavits filed under Rule 75. The affidavits have been reexamined but we find nothing therein except the mere inference that the subject matter in issue here was disclosed to Stones by Coussmaker.

The case of *Ex parte Grosselin* 1901 C. D. 248, is analyzed by applicants in such a way as to contend that this decision never was intended to apply to a case where the printed publication in question was one's own publication. There are, however, certain obiter statements made in the *Grosselin* decision which might be taken to indicate that the provisions of Rule 75 requiring the applicants to show completion of the invention in this country apply to a case wherein the applicant is required to overcome the filing date of his own publication. It is our opinion, however, that these obiter statements are not definite and any such construction of Rule 75 as contended for by the examiner is clearly refuted by the general tenor and intent of the decision. Rule 75 was intended to provide *Ex parte* means by which an applicant can overcome a rejection based on a publication of the invention not more than two years prior to his application. We do not agree with the examiner that this rule is intended to apply to a case where the publication

appears without question to be a publication of the applicant's own invention.

The Commissioner indicates in *Ex parte Grosselin* that the examiner should consider whether the German patent was derived from applicant and was in effect nothing more than a printed publication of *Grosselin's* invention. The decision further indicates that Rule 75 permits an applicant to make an *ex parte* showing of his rights (page 254) and that the whole proceeding is by analogy to the interference practice. On page 253 it is stated that, "Whenever this Office has satisfactory evidence that some other person is as against the applicant entitled to a patent, it is, under the general principles of the law which are well recognized, bound to reject the application."

Applicants' patent in Great Britain has not been sealed so that there is no reason for rejecting the claims under Rule 29 and it appears obvious that applicants made their invention prior to the date of their published specification.

It is our opinion that this record does not show prior invention of the subject matter of the claims by a party other than the applicants. They are, therefore, entitled to a patent.

The decision of the examiner is reversed.

Circuit Court of Appeals, Second Circuit

SHELDON et al. (complainants-appellees)

v.

MOREDALL REALTY CORPORATION (respondent-appellant)

No. 139

Decided Feb. 21, 1938

**Copyrights—Pleading and practice in courts; Appeals to Circuit Courts of Appeals—Orders appealable—**

Trial judge, recognizing non-existence of actual or threatened continued infringement, concluded in opinion that injunction should not issue, but apparently through inadvertence injunction was included in decree; appeal from that part of decree was properly taken; injunction is vacated and decree to that extent reversed; as jurisdiction to review interlocutory decree depends on 28 U. S. C. 227, general rule is that propriety of granting other relief forms no part of subject matter of appeal and is not before Circuit Court of Appeals, not being final decree, but rule is subject to one exception; where such appeal is rightly taken court may examine record thus made to determine whether bill is wholly lacking in equity and, if so, may dismiss; but where doubt exists as to equitable jurisdiction, that matter is left to appeal from final decree.

**Copyrights—Pleading and practice in courts—**

Copyright statute differs from patent and trade mark statutes, and injunction is not condition precedent for accounting and award of damages for copyright infringement; equitable jurisdiction having been invoked in good faith by suitable allegations in bill, jurisdiction may not fall with failure of proof on merits of exclusively equitable rights; nor can court be sure on appeal from interlocutory decree that equity does not have concurrent jurisdiction of accounting on general principles.

**Patents—Jurisdiction of courts—For patent infringement—**

In patent cases, only where injunction is rightly granted may there be accounting and award of damages in equity.



\*\* TX CONFIRMATION REPORT \*\*

AS OF JAN 3 '96 13:32 PAGE.01

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Address: \_\_\_\_\_

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FAX #: \_\_\_\_\_

Contact #: \_\_\_\_\_

From: Name: Daniel P Morris

Phone: \_\_\_\_\_

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: Bednorz et al.

Art Unit: 1105

Serial No.: 08/303,561

Examiner: D. McGinty

Filed: September 9, 1994

Date: January 3, 1996

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

I hereby certify that this paper is being facsimile transmitted under Rule 37  
CFR §1.161(d) to the U.S. Patent and Trademark Office on the date shown  
above.



Daniel P. Morris

Reg. No. 32.053

**SUPPLEMENTARY RESPONSE**

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

In response to the Office Action dated March 29, 1995, please consider the fol-  
lowing:

**REMARKS**

These remarks are in addition to those of the previously submitted response.

As further support for applicants' position that the claims under examination  
are supported by applicants' specification the attached affidavit of Dr. Chang  
C. Tsuei is submitted. Dr. Tsuei's affidavit is in agreement with the earlier  
submitted affidavit of Drs. Donger and Mitzi and states that applicants initi-

ated high temperature superconductor field and the teaching in applicants' specification enables a person of skill in the art to fabricate and use the invention as claimed by applicants.

Claims 24-26, 86-90 and 96-108 have been rejected under 35 USC §102(a) as being anticipated by the Asahi Shinbum article and under 35 USC §103 in view of the Asahi Shinbum article. In addition to applicants' remarks in regard to this rejection in applicant's prior response please consider the following.

The date of the Asahi Shinbum article is November 28, 1986. As stated in applicants' specification at page 6, lines 7-10:

The basis for our invention has been described by us in the following previously published article: J.G. Bednorz and K.A. Muller, Zeitschrift fur Physik B - Condensed Matter, 64, pp. 189-193 Sept. (1986)

The Examiner is using Asahi Shinbum as a reference under 35 USC §102(a). Applicants respectfully disagree since to do so does not permit applicants the one year period provided under 35 USC §102(b) to file a US application after their own publication which permitted applicants to file the present application up to September 1987. The date of the Asahi Shinbum article is after the date of applicants' publication.

Applicants believe this is not a correct application of 35 USC §102. The Court of Custom and Patent Appeal in In re Katz 215 USPQ 14, 17 (a copy of which is attached) states that

It may not be readily apparent from the statutory language that a printed publication cannot stand as a reference under §102(a) unless it is describing the work of another. A literal reading might appear to make a prior patent or printed publication "prior art" even though the disclosure is that of the applicant's own work. However, such an interpretation of this section of the statute would negate the one year period afforded under §102(b)<sup>1</sup> during which an inventor is allowed


to perfect, develop and apply for a patent on his invention and publish descriptions of it if he wishes.

Thus, one's own work is not prior art under §102(a) even though it has been disclosed to the public in a manner or form which otherwise would fall under §102(a). Disclosure to the public of one's own work constitutes a bar to the grant of a patent claiming the subject matter obvious therefrom only when the disclosure occurred more than one year prior to the date of the application, that is, when the disclosure creates a one-year time bar, frequently termed a "statutory bar," to the application under §102(b). As stated by this court in *In re Facius*, 56 CCPA 1348, 1358, 408 F.2d 1396, 1406, 161 USPQ 294, 302 (1969), "But certainly *one's own invention*, whatever the form of disclosure to the public, may not be prior art against oneself, *absent a statutory bar*." [Emphasis in original]<sup>2</sup>.

The Asahi Shinbum article states in the first paragraph:

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phy. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

The "scientists in Switzerland" are the inventors of the above-identified application. The Asahi Shinbum article only reports the work of applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of applicants' "own invention" and cannot be used as a reference. Therefore, the Examiner is respectfully requested to withdraw the rejection of claims 24-26, 86-90 and 96-108 under 35 USC §102(a) as anticipated by Asahi Shinbum and under 35 USC §103 as obvious over Asahi Shinbum.

By:   
Daniel P. Morris  
Registration No. 32,053



電氣抵抗セロ

セラミックス

可抵抗がゼロになる高温等  
現象を、絶対零度三〇度（即ち  
零下約二四三度）の二箇度で  
心起す新セラミックスが発見  
された。今般ニイスの研究が、  
高温超伝導性の可能性を示した  
初度で、このほど東京工大学配  
理工学科の田中徹二教授らのク

ループが破綻し、潰れた。これは実用上で実用されている低圧溶媒材料は絶対腐蝕が起らないでなければならぬ。腐蝕現象が起らないためには、溶剤に高価な特殊なヘリウムを使わなくてはならなかった。新材料はより水素と酸素が強く、安定な液体水素と十分働くので、毎秒上列出た能力損失のなほ遠近などの利用化に必要とされた。また、ミックスはミックスと原料の純化型バリウムが起したのも、ヘロスはパイプとされる三次の超高温で、金属のような耐性を持つ。即ち耐腐蝕性、このミックスの絶対耐腐蝕性、これまで、耐腐蝕材料特有の性能を全く逆さまに完全な腐蝕性（マイ


スナリ効能を保つことを期して、  
超伝導材料は作られた。これに  
一度熱したまま水を流し続け  
ければ、永久電力で強い磁場  
が得られると、利用が非常に  
多くなり、しかし、超伝導現  
象を起す超低温が得られる  
ことがなかった。

すでに用化されている二十  
七元素、元素周期表の最前部  
二の位置で、実験室での最前部  
二元素である、水・二酸化水素、こ  
の超伝導は一九三三年に発見わ  
らなかつた。

現在、用化されている超伝  
導材料は、わずかな物質（液体ヘリ  
ウム）（超流動超伝導度）で冷  
やされている、日本でも作れる  
液体ヘリウムは、金部アメリカ

なかから輸入に頼っている。塩化塩が三〇度になれば、沸点が約四度、一〇度の液体水素や同一七度の液体ネオンの使用が可能となる。

超伝導磁石 医学用の超伝導核磁気共鳴診断装置は、従来の超伝導磁石を更に二倍強に増えているので、高圧で動く超伝導材料の開発は世界中の研究がしのぎを削っている。



from ASAHI SHINKUN

International Satellite Edition

28. 11. 1986 (London)



## DISCOVERY OF NEW SUPERCONDUCTING MATERIAL

" CERAMIC WITH SUFFICIENT SUPERCONDUCTIVE POWER IN  
HIGH TEMPERATURE REGION "

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland in this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.  $T_c$ 's of all superconducting materials which we have in practical application till now are lower than 20K. Therefore we need large amount of liquid He for cooling. Note that the price of liquid He is very expensive. But with this new material we can use cheaper liquid  $H_2$  for cooling. We can expect great from this material to the applications such as linear motorcars, electricity transport systems, etc.

The ceramic newly discovered, is an oxide compound of La and Cu with Ba, which has a structure of the so-called perovskite and shows metal-like properties. Prof. Tanaka's laboratory confirmed that this material shows diamagnetism (Meissner effect) up to 30K, which is the most important indication of the existence of superconductivity.

There are a lot of possibilities for practical applications of superconductors. For example very strong magnets, made of superconducting coils, etc. But one handicap is that  $T_c$  is too low in in each material we know till now.

The  $T_c$  of Nb-alloys which are already in practical use are lower than 20K. The record of  $T_c$  in a laboratory is around 23.2K. This record has not been broken since 1973.

Nowadays each instrument using superconductors is operated by liquid He cooling, and He is a very rare material with a boiling point of 4K. Liquid He used in present Japan is exclusively imported from the USA. If we could get a material with a high  $T_c$  of 30K, we can not only use liquid  $H_2$  but also liquid Ne with a boiling point of 27K.

Since the application of superconductors to many fields, such as very strong magnets, medical use of NMR machines, etc. show rapid increasing, research field of high  $T_c$  superconductivity is high-competitive all over the world.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Bednorz et al.

Art Unit: 1105

Serial No.: 08/303,561

Examiner: D. McGinty

Filed: September 9, 1994

Date: January 2, 1996

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. §1.132

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Chang C. Tsuei, being duly sworn, do hereby depose and state:

That I received a B.S. degree in Mechanical Engineering from National Taiwan University (1960) and M.S. and Ph.D. degrees, in Material Science (1963, 1966) respectively from California Institute of Technology.

That I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York, from 1973 to the present. (See attached Exhibit A for other professional employment history.)

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1973 to the present.

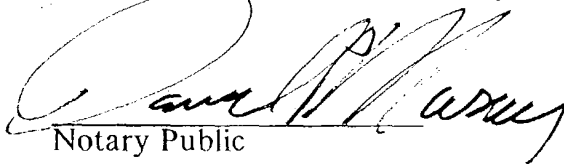
That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by claims 24-26, 86-90 and 96-108, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

By: Chang C. Tsuei  
Chang C. Tsuei

Sworn to before me this 26th day of September, 1995.

  
Notary Public

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4838676  
Qualified in Westchester County  
Commission Expires March 15, 1997

**CHANG C. TSUEI**

**Education**

California Institute of Technology, M.S. (1963), Ph.D. (1966)  
National Taiwan University, B.S. (1960)

**Professional Employment**

1993-present - Research Staff Member  
1983-1993 - Manager, Physics of Structured Materials  
1979-1983 - Manager, Physics of Amorphous Materials  
1974-1975 - Acting Manager, Superconductivity  
1973-1979 - Research Staff Member

Harvard University: 1980 (Summer)  
Visiting Scholar in Applied Physics

Stanford University: 1982 (Sept.) - 1983 (April)  
Visiting Scholar in Applied Physics

California Institute of Technology  
1972 - 1973 - Senior Research Associate in Applied Physics  
1969 - 1972 - Senior Research Fellow in Materials Science  
1966 - 1969 - Research Fellow in Materials Science

sufficient.<sup>5</sup> *Lindstrom v. Ames*, 37 App. D.C. 365, 1911 C.D. 384 (1911) (proof of actual reduction to practice negates having to rely on one's filing date for constructive reduction to practice). See also *Starr v. Farmer*, 1883 C.D. 34, 23 O.G. 2325 (Sec'y Int. 1883), wherein it was held that actual reduction to practice may be better evidence of invention than an application but that "until that evidence [the application] is overthrown," *id.* at 38, the applicant need do more than rely on his application filing date.

In any event, I would remand for determination of Daugherty's right to rely on the date of their application as their priority date or for a determination of priority based on the evidence of Daugherty's actual reduction to practice.

#### Court of Customs and Patent Appeals

In re Katz

No. 82-521

Decided Aug. 27, 1982

#### PATENTS

##### 1. Court of Customs and Patent Appeals — Issues determined — Ex parte patent cases (§28.203)

CCPA treats Section 102(g) rejection that Board of Appeals did not specifically reverse as having been affirmed.

##### 2. Interference — Priority (§41.70)

Section 102(g) embodies principle that to be entitled to patent one must be first to have made invention; however, prior conception of invention by another does not defeat one's

right; no barrier is created by that section unless another has either actually reduced invention to practice or has constructively reduced it to practice by filing patent application.

##### 3. Interference — Priority (§41.70)

###### Interference — Reduction to practice — Constructive reduction (§41.755)

Unlike filing of patent application, publication of article is not constructive reduction to practice of subject matter described in it; therefore, disclosure in publication does not prove that any "invention" within meaning of Section 102(g) has ever been made by anyone.

##### 4. Patentability — Anticipation — Patents — In general (§51.2211)

###### Patentability — Anticipation — Publications — In general (§51.2271)

Interpretation of Section 102(a) that would make prior patent or printed publication "prior art" even though disclosure is that of applicant's own work would negate one year period afforded under Section 102(b) during which inventor is allowed to perfect, develop, and apply for patent on his invention and publish descriptions of it if he wishes.

##### 5. Patentability — Anticipation — In general (§51.201)

One's own work is not prior art under Section 102(a) even though it has been disclosed to public in manner or form that otherwise would fall under Section 102(a); disclosure to public of one's own work constitutes bar to grant of patent claiming subject matter so disclosed, or subject matter obvious from it, only when disclosure occurred more than one year prior to application's date, that is, when disclosure creates one-year time bar to application under Section 102(b); one's own invention, whatever form of disclosure to public, may not be prior art against oneself, absent statutory bar.

##### 6. Patentability — Anticipation — Publications — In general (§51.2211)

Disclosure of publication that occurred less than one year before appellant's application comes within scope of Section 102(a) only if description is not of appellant's own work.

##### 7. Patentability — Anticipation — Publications — In general (§51.2211)

Authorship of article by itself does not raise presumption of inventorship with respect to subject matter disclosed in article; thus, co-authors may not be presumed to be co-inven-

<sup>5</sup> As noted in *Tofe v. Winchell*, *supra* at 61, 209 USPQ at 382 n. 10, only abandonment, suppression or concealment of the invention are grounds under §102(g) for awarding priority *de jure* to the party who is not the first inventor *de facto*. Thus, I disapprove of the view expressed by the board in *Magdo v. Peltzer*, 212 USPQ 838, 845 (BOP1 1981) (on Petition for Rehearing)

a party to an interference who has not complied with the "best mode" requirement of the statute has "no right to make" his claims corresponding to the counts and, therefore, is not entitled to an award of priority, irrespective of testimony as to inventive acts \* \* \*

See also n.3, *supra*.

tors merely other hand, publication claimed in application which it may tion whether ple, if author specifically cant's work content and well as circulation, not considered.

#### 8. Patentation

Although vits or decl. that does inventorshi work in w have been have ended reasonably inventor, t Rule 132, showing position.

#### 9. Application (§14.1)

##### Patentation

Joint in face of sv article au working supervision

##### Particulars

Katz, I ance, reje reversed.

##### Appeal Board of

Applic: Katz, Ser tion, Seri From dec 18, app' Judge, di

John H. of Nev

tors merely from fact of co-authorship; on other hand, when PTO is aware of printed publication that describes subject matter of claimed invention and is published before application is filed (only date of invention on which it must act in absence of other proof), article may or may not raise substantial question whether applicant is inventor; for example, if author, whether he is applicant or not, specifically states that he is describing applicant's work, no question at all is raised; content and nature of printed publication, as well as circumstances surrounding its publication, not merely its authorship, must be considered.

#### 8. Patentability — Anticipation — Publications — In general (§51.2211)

Although submission of disclaiming affidavits or declarations by other authors of article that does not tell anything specific about inventorship and that reports on scientific work in which applicant and other authors have been engaged in some capacity would have ended inquiry into whether it can be reasonably concluded that applicant is sole inventor, they are not required by statute or Rule 132; what is required is reasonable showing supporting basis for applicant's position.

#### 9. Applicants for patent — In general (§14.1)

##### Patentability — Anticipation — Publications — In general (§51.2211)

Joint inventorship cannot be inferred, in face of sworn statements to contrary, from article authored by applicant and students working under applicant's direction and supervision.

##### Particular patents — Immunological Tolerance Induction

Katz, Induction of Immunological Tolerance, rejection of claims 1, 5, 17, and 18 reversed.

Appeal from Patent and Trademark Office Board of Board of Appeals.

Application for patent of David Harvey Katz, Serial No. 937,574, division of application, Serial No. 764,586, filed Feb. 3, 1977. From decision rejecting claims 1, 5, 17, and 18, applicant appeals. Reversed; Miller, Judge, dissenting with opinion.

John H. Lynn and Grant L. Hubbard, both of Newport Beach, Calif., for appellant.

Joseph F. Nakamura and Gerald H. Bjorge for Patent and Trademark Office.

Markey, Chief Judge, and Rich, Baldwin, Miller, and Nies, Associate Judges.

Nies, Judge.

This appeal is from the decision of the Patent and Trademark Office (PTO) Board of Appeals (board) sustaining rejection of claims 1, 5, 17, and 18, all remaining claims in application Serial No. 937,574 for "Induction of Immunological Tolerance." The subject application is a divisional application of application Serial No. 764,586, filed February 3, 1977, and is entitled to that filing date. The claims were rejected because of a description of the subject matter of the invention in a publication dated June 1976, which appellant, however, asserts is a description of his own work. The board was unpersuaded by appellant's declarations to that effect and sustained the rejection. We reverse.

#### Background

In June, 1976, eight months before appellant's effective filing date, an article coauthored by Nicholas Chiorazzi, Zelig Eshhar and appellant was published in the Proceedings of the National Academy of Science, U.S.A., Vol. 73, No. 6, pp. 2091-95. There is no dispute that the article (Chiorazzi et al.) fully describes the claimed invention.

Along with his divisional application, appellant filed a declaration in which he declared that:

He is the sole inventor of the subject matter described and claimed in the United States Patent Application Serial No. 764,586, filed February 3, 1977, entitled, INDUCTION OF IMMUNOLOGICAL TOLERANCE, which subject matter is disclosed and claimed in part in the divisional application with which this declaration is submitted.

He is co-author of a report in the proceedings of the National Academy of Science, U.S.A., Volume 73, No. 6, Pages 2091-2095, June, 1976, communicated to the National Academy of Science by Albert H. Coons, a member of said Academy, on March 8, 1976, that he is the sole inventor of the subject matter which is disclosed in said publication in the proceedings of the National Academy of Science and disclosed and claimed in the application submitted herewith. [Emphasis ours.]

The other authors of the publication, Nicholas Chiorazzi and Zelig Eshhar were students working under the direction and supervision of the inventor, Dr. David H. Katz, and while co-authoring the publication, are not co-inventors of the subject matter described therein.

#### The Examiner's Rejections

In his first Official Action, the examiner stated:

Claims 1, 5, 17 and 18 are rejected under 35 USC 102(g) as anticipated by Chiorazzi et al. \*\*\* Applicant's declaration \*\*\* is entirely ineffective in overcoming the rejection of this nature and is considered to be nothing more than the self-serving statement.

In his Final Official Action, the examiner adhered to the §102(g) rejection adding:

[T]here is no evidence of record which makes it clear that appellant is the sole inventor of the claimed invention \*\*\*. Where a reference is from a collection of authors, it must be assumed that all authors contributed equally even though it is recognized that sometimes individuals involved only with assay and testing features of the invention and \*\*\* not involved in the conceptual [sic] aspect of the research are included as an author to a particular reference. There is not sufficient evidence of record to show that applicant is the sole inventor of the claimed invention.

\* \* \*

\*\*\* The publication date as well as communication date of the reference, both dates being prior to applicant's filing date, [are] clear evidence to [sic] prior invention. [Emphasis in original].

To overcome the rejection, the examiner required that appellant either (1) amend his application to include the other authors as coinventors, or (2) file affidavits from the other authors "disclaiming the invention claimed." Appellant chose to appeal rather than comply with either requirement.

#### The Board's Affirmance

While the board sustained the examiner's rejection, it did so on the following ground:

The Chiorazzi et al. article, as pointed out by the examiner and as acknowledged by appellant, fully describes the presently claimed therapeutic immunosuppressive agent and the method of preparing same. In view of the fact that the article was published some eight months prior to the effective filing date of the present application and since the authors of the article are legally another within the meaning of Section 102(a), we are satisfied that the examiner has clearly established a prima facie case of lack of novelty of the presently claimed therapeutic agent and method.

Appellant, who is a coauthor of the Chiorazzi article, has stated under oath that he is the sole inventor of the subject matter herein claimed and described in the article, and that the other authors, namely, Chiorazzi and Eshhar, are not coinventors but were simply students working under his direction and supervision. In appellant's view, this declaration constitutes legally acceptable evidence and, in the absence of evidence to the contrary, is sufficient to establish that he is the sole inventor of the subject matter in issue.

However, we do not find this declaration, standing alone, sufficient to establish that Katz is the sole inventor and thus remove the Chiorazzi article as a reference against the presently claimed subject matter. Although appellant may be of the opinion that he is the sole inventor, such a view may not be shared by the coauthors of this article. Coauthors Chiorazzi and Eshhar may, in fact, be of the opinion that they are, at the very least, coinventors of the subject matter described in the article and claimed herein. Even though authorship may not conclusively establish inventorship, it is reasonable to infer that such a relationship exists. Appellant's unsupported statement, even though under oath, does not convince us otherwise. In our view, disclaiming affidavits or declarations by the other authors are required in order to support appellant's contention that he is the sole inventor of the subject matter described in the Chiorazzi article and claimed here. [Emphasis ours.]

The board adhered to its position on rehearing.

#### Opinion

[1] Because the board did not specifically reverse the §102(g) rejection, we treat it as having been affirmed. 37 CFR 1.196(a). Fur-

ther, since a board's reliance for rejection. 37 CFR 1.102(e) with reference to thors of agree that respect for ent and, acc to consider

#### [2] Section

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[3] We position the article pro rejection u filing of a of an arti reduction described t 986, 989, 2 305-06 (1- publication tion" with been mad ground for

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ther, since appellant does not contend that the board's reliance on §102(a) is a new ground for rejection, we will also consider that section. 37 CFR 1.196(b). Appellant does suggest that the board apparently confused §102(c) with §102(a) since §102(a) makes no reference to "another" in the context of authorship of a publication. However, we disagree that the board was "confused" in this respect for reasons which will become apparent and, accordingly, do not find it necessary to consider §102(c) separately.

### 35 USC 102(g)

[2] Section 102(g) reads:

A person shall be entitled to a patent unless —

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(g) before the applicant's invention thereof the invention was made in this country by another who had not abandoned, suppressed, or concealed it. In determining priority of invention there shall be considered not only the respective dates of conception and reduction to practice of the invention, but also the reasonable diligence of one who was first to conceive and last to reduce to practice, from a time prior to conception by the other.

This section of the statute embodies the principle that to be entitled to a patent one must be the first to have made the invention. However, prior conception of the invention by another does not defeat one's right. No possible barrier is created by §102(g) unless another has either actually reduced the invention to practice or has constructively reduced it to practice by filing a patent application.

[3] We specifically reject the examiner's position that the publication of the subject article provides even a tenuous ground for rejection under 35 USC 102(g). Unlike the filing of a patent application, the publication of an article is not deemed a constructive reduction to practice of the subject matter described therein. In *re Schlittler*, 43 CCPA 986, 989, 234 F.2d 882, 884, 110 USPQ 304, 305-06 (1956). Therefore, disclosure in a publication does not prove that any "invention" within the meaning of 102(g) has ever been made by anyone. The examiner's ground for rejection must, therefore, fail.

### 35 USC 102(a)

Section 102(a) reads:

A person shall be entitled to a patent unless —

(a) the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicant for patent.

[4] It may not be readily apparent from the statutory language that a printed publication cannot stand as a reference under §102(a) unless it is describing the work of another. A literal reading might appear to make a prior patent or printed publication "prior art" even though the disclosure is that of the applicant's own work. However, such an interpretation of this section of the statute would negate the one year period afforded under §102(b) during which an inventor is allowed to perfect, develop and apply for a patent on his invention and publish descriptions of it if he wishes. *Illinois Tool v. Solo Cup Co.*, 461 F.2d 265, 172 USPQ 385 (CA 7), cert. denied, 407 U.S. 916 (1972).

[5] Thus, one's own work is not prior art under §102(a) even though it has been disclosed to the public in a manner or form which otherwise would fall under §102(a). Disclosure to the public of one's own work constitutes a bar to the grant of a patent claiming the subject matter so disclosed (or subject matter obvious therefrom) only when the disclosure occurred more than one year prior to the date of the application, that is, when the disclosure creates a one-year time bar, frequently termed a "statutory bar," to the application under §102(b). As stated by this court in *In re Facius*, 56 CCPA 1348, 1358, 408 F.2d 1396, 1406, 161 USPQ 294, 302 (1969), "But certainly one's own invention, whatever the form of disclosure to the public, may not be prior art against oneself, absent a statutory bar." [Emphasis in original.]<sup>2</sup>

<sup>1</sup> 35 USC 102(b) provides:

A person shall be entitled to a patent unless —

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(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States. [Emphasis added.]

<sup>2</sup> Since any valid rejection is necessarily a "statutory bar," in a generic sense, the expression "statutory bar" must be understood here as meaning "statutory time bar" under 35 USC 102(b).



[6] Since the publication in this case occurred less than one year before appellant's application, the disclosure comes within the scope of §102(a) only if the description is not of appellant's own work.

The specific question present in this appeal is essentially an evidentiary one, namely, the sufficiency of applicant's showing to establish that the subject disclosure was his original work, and his alone.<sup>3</sup> We conclude that appellant's declaration is sufficient in this case to overcome the rejection.

[7] As an initial matter, we hold that authorship of an article by itself does not raise a presumption of inventorship with respect to the subject matter disclosed in the article. Thus, co-authors may not be presumed to be coinventors merely from the fact of co-authorship. On the other hand, when the PTO is aware of a printed publication, which describes the subject matter of the claimed invention and is published before an application is filed (the only date of invention on which it must act in the absence of other proof), the article may or may not raise a substantial question whether the applicant is the inventor. For example, if the author (whether he is the applicant or not) specifically states that he is describing the work of the applicant, no question at all is raised. The content and nature of the printed publication, as well as the circumstances surrounding its publication, not merely its authorship, must be considered.

What we have in this case is ambiguity created by the printed publication.<sup>4</sup> The article does not tell us anything specific about inventorship, and appellant is only one of three authors who are reporting on scientific work in which they have all been engaged in some capacity at the Harvard Medical School. It was incumbent, therefore, on appellant to provide a satisfactory showing which would lead to a reasonable conclusion that he is the sole inventor.

<sup>3</sup>Such showing can be made under Rule 132, 37 CFR 1.132, which provides:

When any claim of an application is rejected on reference to a \*\*\* printed publication \*\*\* affidavits or declarations traversing [the reference] \*\*\* may be received.

<sup>4</sup>The solicitor notes that in the application, there is an inconsistency in that the subject application and its parent by a sole inventor refer to previous work done by "one of the inventors." While adding to the ambiguity, this statement, which appellant's attorney represents was his error in draftsmanship, does not control over appellant's subsequent proofs.

[8] The board and the examiner held that "disclaiming affidavits or declarations by the other authors are required to support appellant's position that he is, in fact, the sole inventor of the subject matter described in the article and claimed herein." This was clear error. Submission of such affidavits or declarations would have ended the inquiry, but we do not agree that they are required by the statute or Rule 132. What is required is a reasonable showing supporting the basis for the applicant's position.

In this case, appellant reaverred in his declaration that he is the sole inventor of the subject matter described and claimed in his application and also that disclosed in the publication of proceedings of the National Academy of Science. We do not view this averment as a mere pro forma restatement of the oath in his application.

[9] In the declaration, appellant provides the explanation that the co-authors of the publication, Chiorazzi and Eshhar, "were students working under the direction and supervision of the inventor, Dr. David H. Katz." This statement is of significance since it provides a clear alternative conclusion to the board's inference that their names were on the article because they were coinventors. As acknowledged by the examiner, the names of individuals may be given as authors of a scientific report who are "involved only with assay and testing features of the invention." Appellant's explanation is, thus, consistent not only with the content of the article but with the nature of the publication. On the record here, the board should not have engaged in further speculation as to whether appellant's view was shared by his co-authors but rather should have accepted that Chiorazzi and Eshhar were acting in the capacity indicated, that is, students working under the direction and supervision of appellant. From such a relationship, joint inventorship cannot be inferred in the face of sworn statements to the contrary.

Thus, we conclude that in view of the totality of circumstances, appellant has made a sufficient showing that the cited publication discloses his invention. Accordingly, we reverse the decision of the board.

Reversed.

Miller, Judge, dissenting.

The board correctly held that it is reasonable to infer coinventorship from coauthor-

ship. This determination printed publication question is applied against by one of CCPA 134 (1969); In F.2d 1393 Land, 54 USPQ 621 opinions by patents issued the board involving (Magner, 131 USPQ 384 (1943). Sustained appeal arguments, at

In Layne, the board held that an argument made with sufficient evidence. The board

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<sup>5</sup>As argued, the invention is also evidenced by the prior art in a printed publication of the invention under 102(a) and, that "before" the invention was made under 35 USC "not himself" are terms that inventive entity's view of indicates that practice; appropriate rejection on applicant, is a date of invention application filed and Eshhar & CHISUM OF

ship. This inference is sufficient to justify a determination by the PTO that the reference printed publication ("Chiorazzi et al.") in question is prior art under 35 USC 102 as applied against an application for patent filed by one of the coauthors.<sup>1</sup> In re Facius, 56 CCPA 1348, 408 F.2d 1396, 161 USPQ 294 (1969); In re Mathews, 56 CCPA 1033, 408 F.2d 1393, 161 USPQ 276 (1969); In re Land, 54 CCPA 806, 368 F.2d 866, 151 USPQ 621 (1966). Although all of the latter opinions by this court have involved prior patents issued to different inventive entities, the board has established a line of cases involving only printed publications. In re Magner, 133 USPQ 404 (1961); In re Seaborg, 131 USPQ 202 (1960); In re Hirschler, 110 USPQ 384 (1952); In re Layne, 63 USPQ 17 (1943). Such cases are analogous to the instant appeal, and, contrary to appellant's arguments, are consistent.

In Layne, the board agreed with the examiner that an affidavit by the applicant, stating that an article published by another was made with the applicant's consent, was not sufficient to overcome the examiner's rejection. The board stated:

[I]t is stated in the brief that counsel can obtain an affidavit of the writer of the article in the publication that he obtained his information from the deponent. It is our view that this affidavit of the writer of the article, H. Lee Flood, should be furnished to afford complete and satisfactory proof of the identity of the article disclosed in the publication.

\*\*\*[U]ntil the affidavit referred to is furnished, the rejection on the publication in the Petroleum Engineer appears proper.

<sup>1</sup> As argued by the Solicitor, this printed publication is also evidence that "the invention was known or used by others in this country \*\*\* or described in a printed publication in this \*\*\* country, before the invention thereof by applicant" under 35 USC 102(a) and, as held by the examiner, is evidence that "before the applicant's invention thereof the invention was made in this country by another" under 35 USC 102(g). The "others" in 102(a), "not himself" in 102(f), and "another" in 102(g) are terms that serve to distinguish between different inventive entities. Contrary to the majority opinion's view of section 102(g), the Katz et al. article indicates that the invention was actually reduced to practice; appellant did not contest the examiner's rejection on this basis. In this case, Katz, the applicant, is one inventive entity and his effective date of invention, as the record now stands, is his application filing date. Collectively, Katz, Chiorazzi, and Eshhar comprise a second inventive entity. See CHISUM ON PATENTS §3.08[2](a).

For this reason, the rejection is affirmed. It is recommended, however that if a proper affidavit of H. Lee Flood is promptly submitted, the claims be allowed.

63 USPQ at 19. Layne differs from the present case in that the inventor in Layne was not named as a coauthor; here, Katz was one of the named coauthors.

When presented with an examiner's rejection utilizing a publication coauthored by the applicant and his laboratory assistant, the board in Hirschler refused to sustain the rejection in view of the submission of an affidavit disclaiming inventorship which was executed by the lab assistant. The board said:

[A]n affidavit which points out that affiant took no part in writing the article and was not the inventor of the subject matter described in the article, but was merely listed as coauthor of the article in order to receive credit for having collaborated on the research program under the directions of present appellant, is properly acceptable and \*\*\* the article may be considered the sole work of present appellant. Since the article is not a statutory bar, it is not effective as a reference.

110 USPQ at 387. Here, of course, there are no disclaiming affidavits filed by the coauthors and alleged noninventors.

Appellant quotes the following statement of the board in Seaborg explaining that a Rule 131 affidavit was unnecessary:

The issue is not one of priority but attribution of inventorship, the examiner evidently having in mind the possibility that Wahl might be a joint inventor. But we would emphasize that the bare fact that Wahl is the literary co-author is not evidence of joint inventorship.

131 USPQ at 203. This statement is taken out of context, the board actually concluding:

On the question of originality any evidence convincing to the Office may be accepted. The evidence here is in the form of an affidavit by joint author Wahl stating that he is not the inventor of the subject matter claimed herein. In absence of any adversity of interest there seems to be little basis for challenging this affidavit. In fact, the examiner states on page 4 of his answer that he "has no doubt that Seaborg is the sole inventor of the subject matter claimed."

Under these circumstances we see no valid basis for maintaining the rejection on the Seaborg and Wahl article.

131 USPQ at 203. As is apparent, a disclaiming affidavit was filed by the coauthor and noninventor, which clearly distinguishes Seaborg from the present case. Also, the board justified its position, at least in part, on the basis that the affiant had no "adversity of interest."

In *Magner*, three of four applicants had published an article disclosing their invention less than a year prior to the application's filing date. The three coauthors and coinventors filed an affidavit declaring that the fourth applicant was also a coinventor, viz., that he "and themselves mutually participated in the conception, research and reduction to practice of the invention claimed \*\*\*" and that the article "was prepared from the research records of themselves and the fourth coinventor." 133 USPQ at 405. The examiner refused to accept this affidavit because an explanatory affidavit by the fourth coinventor had not been presented. The board refused to sustain the examiner's rejection, stating:

The article is by three of the four joint inventors; we see no necessity for an affidavit under Rule 131 as no question of priority is involved. The question is as to attribution of inventorship — an explanation of the relation of the publication by three of the joint inventors to the application of all four of them. We think that the affidavit satisfies this requirement. On the question of originality any competent evidence convincing to the Office may be accepted. *There is no reason to doubt the statement of the three joint inventors as to the participation of the fourth inventor as this statement is of no benefit to them.* [Emphasis supplied.]

*Id.* This is unlike the present case, where the appellant's affidavit is favorable to his own interest and adverse to the interests of coauthors Chiorazzi and Eshhar.

Appellant argues that the board's reasoning in *In re McGuckian*, 202 USPQ 398 (1975), is somehow analogous and supports his position. *McGuckian*, however, involved the use of a typical 37 CFR 1.131 affidavit filed to overcome the examiner's application of a United States Patent as a reference under 35 USC 102(e). The examiner determined that the Rule 131 showing, which included three declarations, two by applicant and one by his attorney, and fifteen exhibits, was not sufficient to meet the requirements of the

rule. The board held that the Rule 131 showing was sufficient and indicated that the examiner was required to accept as true the applicant's sworn statements that "he is the inventor"; that "he conceived and reduced to practice the invention"; and the work evidenced by Exhibits 1 through 15 "was made through his efforts and others at his request on his behalf." In this context, as quoted by Katz, the board said:

It is neither the Examiner's function nor our function under such circumstances to divine the role if any played by someone who is a complete stranger to the proceeding. It is only in some inter partes proceeding, totally lacking here, where all interested parties are represented and the fundamental safeguards of direct examination and cross-examination are possible, that the question of inventorship and dates of invention can be explored in the manner attempted by the Examiner here.

202 USPQ at 399. However, *McGuckian* offers no support to appellant. That case was concerned only with the adequacy of the applicant's Rule 131 showing; whereas, appellant here has not attempted to comply with the requirements of Rule 131.

Essentially, appellant argues that this court either should hold that coauthorship is not evidence of, or a basis for inferring, coinventorship or should accept without question an affidavit by an applicant which simply states that he is the sole inventor. To the contrary, I would hold that coauthorship is evidence of coinventorship and creates an inference thereof which is sufficient to establish a prima facie case under either 35 USC 102(a), (f), or (g) that the Chiorazzi et al. article is prior art;<sup>2</sup> further, that appellant's declaration does not rebut the prima facie case.<sup>3</sup>

As to the showing that would be sufficient to overcome the government's prima facie case, it is to be noted that inventorship is a matter of law which depends upon factual matters underlying the development of the invention, including the contribution by all parties involved with the claimed invention. See *Linkow v. Linkow*, 517 F.2d 1370, 186 USPQ 223 (CCPA 1975); *Hedgewick v.*

<sup>2</sup> See note 1, *supra*.

<sup>3</sup> If Chiorazzi and Eshhar were merely involved in assembling data, conducting experiments, testing the invention, or reporting the inventor's activities, it is not unreasonable to require that this limited role be affirmed by them or Katz. After all, the resources of the PTO are limited and such information is readily available to appellant.

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Akers, 497 F.2d 905, 182 USPQ 167 (CCPA 1974). As related earlier, the board's decision to accept or reject affidavits affecting a nonaffiant's rights in an invention has been predicated upon whether the affiant's statements are adverse to the nonaffiant's interest. Because the affiant, Katz, seeks to adversely affect the interests of the coauthors Chiorazzi and Eshhar, the PTO has refused to accept his affidavit as determinative, leaving him a choice of submitting affidavits by Chiorazzi and Eshhar disclaiming any interest in the invention or making a showing of facts in existence prior to the date of publication of the Chiorazzi et al. article sufficient to prove that inventorship of the claimed invention lies solely with Katz.<sup>4</sup>

The majority accepts the Katz declaration, which simply concludes that Katz is the sole inventor and that his coauthors were students in his employ. Katz has not provided *either* a recitation of facts to support these conclusions, viz., type of supervision in the lab, circumstances resulting in his conception, instructions to his coauthors, participation and performance by his coauthors, etc. *or* a recitation of facts from which the PTO could conclude that his coauthors played no role in the conception of the invention. Joint publication of this article in the names of Katz, Chiorazzi, and Eshhar, without explanation, places a cloud upon the sole application of Katz and requires that Katz affirmatively clear the air. This he has not done.

In view of the PTO's limited resources for processing in excess of 100,000 patent applications a year, it is disappointing that a majority of this court cannot see its way to extend a helping hand to the effort of a vital administrative agency to protect the integrity of the patent system, with minimal inconvenience to an applicant.

## Court of Appeals, District of Columbia Circuit

Oetiker  
v. Jurid Werke GMBH

Nos. 81-1427 and 81-1489

Decided Feb. 19, 1982

### UNFAIR COMPETITION

#### 1. Antitrust laws (§68.15)

One guilty of fraudulent procurement, and attempted enforcement of patent thus procured, may be liable for treble damages to competitors under antitrust laws; enforcement of patent procured by fraud on PTO may be violative of Sherman Act Section 2 provided all other elements necessary to establish Section 2 violation are proved, and persons injured by that violation may sue for treble damages under Section 4 of Clayton Act.

### PATENTS

#### 2. Presumption from patent grant — Patent Office consideration of prior art (§55.5)

Fact that examiner did not apply references is certainly not indication that he misunderstood them.

#### 3. Pleading and practice in Patent Office — In general (§54.1)

Applicant bears no obligation to distinguish over references of record that are not applied against claims.

#### 4. Defenses — Fraud (§30.05)

Patent Office loses all jurisdiction once patent issues, and there can thus be no fraud on Patent Office for failure to cite prior art that was discovered only after issuance of patent.

#### 5. Defenses — Fraud (§30.05)

Finding that patent was procured by fraud must be based on clear, unequivocal, and convincing evidence; there must be evidence of deliberate misrepresentation in PTO; good faith judgment not to cite prior art to PTO, even if erroneous, cannot be fraud; it is necessary that there be clear evidence of specific intent, and that defendant knowingly and willfully misrepresented facts to PTO.

#### 6. Costs — Attorney's fees (§25.5)

35 U.S.C. 285 permits award of attorney's fees in patent cases involving exceptional circumstances.

<sup>4</sup> See U.S. Patent & Trademark Office, Manual of Patent Examining Procedure §715.01(c) (4th Ed. Rev. 1980).

PLEASE STAMP & RETURN TO US

In re application of: Bednorz et al.  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...  
Serial No. 08/303,561 Docket No.:Y0987-074BY Attny:DPM  
Received in the U.S. Patent & Trademark Office:

Supplementary Amendment  
Certificate of Mailing

CHARGED ON OUR ACCOUNT NO.: 09-0468

PLEASE STAMP & RETURN TO US

In re application of: Bednorz et al.  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...  
Serial No. 08/303,561 Docket No.:Y0987-074BY Attny:DPM  
Received in the U.S. Patent & Trademark Office:

Supplementary Amendment  
Certificate of Mailing



ALL FEES ARE TO BE CHARGED ON OUR ACCOUNT NO.: 09-0468

Date of Deposit: October <sup>10</sup> 1995

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Date: October 10, 1995

**Bednorz et al.**

Group No.: 1105

Serial No.: 08/303,561

Examiner: D. McGinty

Filed: September 9, 1994

Docket No. YO987-074BY

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)**

I hereby certify that the attached correspondence comprising:

Supplementary Amendment  
Acknowledgement Card

being deposited with the United States Postal Service as first class mail in an envelope  
addressed to:

**Commissioner of Patents and Trademarks**

**Washington, DC 20231**

on October 10, 1995

Michele Ahl  
(Print name of person mailing paper)

*Michele Ahl*  
(Signature of person mailing paper)

Docket No. YO987-074BY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al. : Date: October 4, 1995  
Serial No.: 08/303,561 : Group Art Unit: 1105  
Filed: September 9, 1994 : Examiner: D. McGinty  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

SUPPLEMENTARY AMENDMENT

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

In response to the office action dated March 29, 1995, please  
consider the following:

REMARKS

The Examiner has cited Asahi Shinbun, International Satellite  
Edition (London), November 28, 1986. Claims 24-26, 86-90, 96-108  
have been rejected as anticipated by Asahi Shinbun under 35 U.S.C.  
102 (a) and as obvious over Asahi Shinbun under 35 U.S.C. 103.

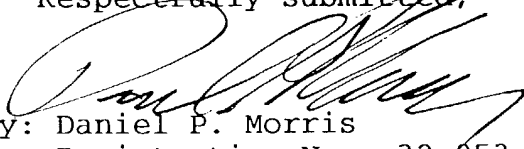
At page 6, lines 7-10 of the specification states that "The  
basis for our invention has been described by us in the following  
previously published article: J.G. Bednorz and K.A. Müller,  
Zeitschrift für Physik B - Condensed Matter, 64, pp. 189-193,

S.N. 08/303,561

September 1986." The present application was filed within a year of this article.

The Asahi Shinbun article reports on applicants' work and says that it has been reproduced by Professor Tanaka. It is therefore not a proper reference, since it is essentially applicants' work.

Respectfully submitted,



By: Daniel P. Morris  
Registration No.: 32,053  
Tel. No. (914) 945-3217

IBM Corporation  
Intellectual Property Law Dept.  
P. O. Box 218  
Yorktown Heights, New York 10598

/ma



PLEASE STAMP & RETURN TO US

In re application of:        Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGHT TRANSITION...

Serial No.08/303,561    Docket No.: Y0987-074BY        Attny:DPM

Received in the U.S. Patent & Trademark Office:

Associate Power of Attorney for DPM, Wllm B.Porter, Wm.Ellis

Petition and Fee for Extension of Time (3mo.)

Affidavits from Dr. T. Dinger and Dr. D. Mitzi

Submission after Final rejection Under 37 CFR 1.129(a)

Appendix A, B, C and D

Amendment

ALL FEES ARE CHARGED TO OUR ACCOUNT NO.: 09-0468

Date of Deposit:

September 26, 1995

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Date: September 26, 1995

Bednorz et al.

Group No. 1105

Serial No.: 08/303,561

Examiner: D. McGinty

Filed: September 9, 1994

Docket No. YO987-074BY

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)**

I hereby certify that the attached correspondence comprising:

Petition and Fee for Extension of Time  
Submission after Final Rejection  
Under 37 CFR 1.129(a)  
Associate Power of Attorney for:  
Daniel P. Morris, William T. Ellis and  
William B. Porter  
Affidavits from Dr. T. Dinger and  
Dr. D. Mitzi  
Amendment  
Appendix A, B, C & D  
Acknowledgement Card

being deposited with the United States Postal Service as first class mail in an envelope  
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**Commissioner of Patents and Trademarks**

**Washington, DC 20231**

on September 26, 1995

Daniel P. Morris

(Print name of person mailing paper)



(Signature of person mailing paper)

Docket No. YO987-074BY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al. : Date: September 26, 1995  
Serial No.: 08/303,561 : Group Art Unit: 1105  
Filed: September 9, 1994 : Examiner: D. McGinty  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AMENDMENT

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

In response to the office action dated March 29, 1995, please  
consider the following:

REMARKS

Claims 24-26, 86-90, 96-108 are in the application.

In view of the remarks herein, the Examiner is respectfully  
requested to reconsider the above-identified application.

Claim of Priority

The Examiner acknowledges applicants' claim for priority under 35 USC 119. The Examiner states "however, a review of that certified copy, which is in English, indicates that it does not support the present assertion of priority. Support is not found in that certified copy for the invention as presently claimed."

Applicants respectfully disagree. The certified copy is directed to transition metal oxide superconducting materials.

A copy of the European Patent Application number 87100961.9, filed January 23, 1987 corresponding to the priority document is attached as Appendix A. Moreover, the title of the priority document refers to "superconductive compounds ... having a high transition temperature" and further provides examples of transition temperatures greater than 26°K." (see for example column 4, lines 56-58 and column 5, lines 7-8).

The Examiner's attention is directed to the following comments from this document which is referred to herein as the priority document.

- I) The priority document states at column 1, lines 7-19 that:

"The present invention proposes to use compounds having a layer-type structure of the kind known from potassium nickel fluoride  $K_2NiF_4$ . This structure is in particular present in oxides of the general composition  $RE_2TMO_4$ , wherein RE stands for the rare earths (lanthanides) and TM stands for the so-called transition metals. It is a characteristic of the present invention that in the compounds in question, the RE portion is partially substituted by one member of the alkaline earth group of metals or by a combination of the members of this alkaline earth group, and that the oxygen content is at a deficit."

- II) The priority document further states at column 3, lines 39-40, "a first layer-type perovskite-like phase, related to the  $K_2NiF_4$

structure".

III) The priority document defines  $T_c$  at column 6, lines 4-5, by referring to the onset of superconductivity, i.e., the value of the critical temperature  $T_c$ ".

IV) The priority document further states at column 6, lines 38-43 that "[r]esistivity... measurements, as a function of temperature... show the same general tendency... A drop in resistivity  $p(T)$ , and a cross-over to diamagnetism at a slightly lower temperature."

V) It is generally known that: "[a] magnetic field... cannot penetrate onto the interior of a superconductor... [p]erfect conductivity implies a time-independent magnetic field in the interior... In a superconductor, the field is not only independent of time, but also zero." (Solid State Physics, N.W. Ashcroft, N.D. Mermin, Saunders College, 1976) (see Appendix B).

VI) It is also well-known that: "[i]n the ideal

case the resistance vanishes completely and discontinuously at a transition temperature. Ts... Actually, the resistance temperature curve does fall more sharply the more the specimen is like a single crystal... [T]he drop always occurs in a measurable temperature range..." (Theory of Superconductivity, M. von Laue, Academic Press, Inc., 1952) (see Appendix C).

Applicants' claim 103 recites (claims 104-108 depend from claim 103):

- A) "providing a superconductor element made of a superconductive composition, the superconductive composition consisting essentially of a copper-oxide compound having a layer-type perovskite-like crystal structure, the copper-oxide compound including at least one rare-earth or rare-earth-like element, and at least one alkaline-earth element".

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B) "composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature change between an upper limit defined by a transition-onset temperature  $T_c$  and a lower limit defined by an effectively-zero-bulk-resistivity intercept temperature  $T_c$ , the transition-onset temperature  $T_c$  being] greater than 26 K".

Support for that part of claim 103 designated as A above is found in the priority document as indicated in I and II above.

Support for that part of claim 103, designated as B above can be found in the priority document in III, IV and V above and in VI above which provides a more detailed explanation of aspects of superconductors as described in the priority document above.

Claim 87 depends from independent claim 86. Support for claims 86 and 87 is found in the priority document in the same way as is support for claims 103-108. Claims 88-89 depend from claim 88. Support for claim 88 is found in the priority document in the same way as for claims 103-108. Claims 97-102 depend from claim



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96. Support for claims 96-102 is found in the priority document in the same way as in found for claims 103-108. Claims 25-26 depend from claim 24. Support for claim 24 is found in the priority document in the same way as is found for claims 103-108.

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Objection to Specification and Rejection of Claims 103-108 Under 35  
USC 112 - Lack of Support

The specification has been objected to under 35 USC 112, first paragraph. The Examiner states that "the language of claim 103 is not supported by the original specification."

Applicants respectfully disagree. Claim 103 is adequately supported by the original specification. As noted above, claim 103 is supported by the priority document.

The Examiner's attention is directed to the following comments from the specification.

VII) The specification states at page 1, lines 5-10, that "This invention relates to ... superconducting compositions including copper and/or transition metals."

The specification further states at page 5, lines 2-9 that:

"It is another object of the present invention to provide novel superconductive materials that are

multi-valent oxides including transition metals, the compositions having a perovskite-like structure."

It is a further object of the present invention to provide novel superconductive compositions that are oxides including rare earth and/or rare earth-like atoms, together with copper or other transition metals that can exhibit mixed valent behavior."

The specification further states at page 8, lines 1-11, that

"[A]n example of a superconductive composition having high  $T_c$  is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically

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elements 58-71 of the periodic table, including Ce, Nd, etc. If an alkaline earth element (AE) were also present, the composition would be represented by the general formula RE-AE-TM-O."

And at page 7, lines 14-15, the specification states that "the rare earths site can also include alkaline earth elements."

The specification at page 6, lines 7-10 states that:

VIII) "The basis for our invention has been described by us in the following previously published article: J.G.Bednorz and K.A. Muller, Zeitschrift für Physik B - Condensed Matter, 64, pp. 189-193, (September 1986)." Another article of interest by us is J.G. Bednorz, K.A. Muller, M. Takashige, Europhysics Letters, 3(3), pp. 379-385 (1987)."

The first article clearly shows in the figures (for example Figure 3 that the resistivity reaches a critical temperature at

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which it begins to rapidly drop and over a small temperature range goes to zero.

Support for recitation A, above of claims 103-108 can be found in the specification as indicated in VII above. Support for recitation B, above of claims 103-108 can be found in the specification as indicated in VIII above.

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Objection to Specification and Rejection of Claims Under 35 USC 112, First Paragraph - Enablement

Claims 103-108 have been rejected under 35 USC 112, first paragraph for the reasons set forth in the objections to the specification. Claims 104-108 depend from claim 103. In view of to applicants' comments in regards to the objection to the specification, the Examiner is respectfully requested to withdraw the rejection of claims 103-108 under 35 USC 112.

The specification has been rejection under 35 USC 112, first paragraph as failing to provide an enabling disclosure commensurate with the scope of the claims. The Examiner states that "the present specification is only enabled for compositions comprising  $Ba_xLa_{5-x}Cu_5O_y$ . The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases."

The Examiner cites number of see CCPA cases in support of the rejection of claims 103-108 under 35 USC 112, first paragraph: in re Fisher, 166 USPQ 18; in re Angstadt and Griffen, 190 USPQ 214, and in re Coliani, 195 USPQ 150.

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Applicants respectfully disagree that claims 103-108 are not enabled by the specification.

The specification at page 8, line 1, states that "An example of a superconductive composition having high  $T_c$  is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr, etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare-earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc. If an alkaline earth element (AE) were also present, the composition would be represented by the general formula RE-AE-TM-O."

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The specification further states at page 11, lines 19-24, that "An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition  $RE_2TMO_4$ , where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal."

The composition  $RE_2TMO_4:RE$  is referred to at page 24, lines 5-9;  $RE_{2-x}TM_xO_{4-y}$  is referred to at page 25, lines 19-21.

The following specific compounds are recited in the application:

$Ba_4La_{5-x}Cu_5O_{5(3-y)}$  at page 10, lines 4, 10, 14. Other compounds are given in the articles to B. Raveau, in Mat. Res. Bull., Vol. 20 (1985) pp. 667-671, and to C. Michel et al. in Rev. Claim. Min. 21 (1984) 407, both of which are incorporated by reference at page 13, lines 4-5.

$La_{2-x}Ba_xCuO_{4-y}$  at page 12, line 13

$La_{2-x}Ba_xNiO_{4-y}$  at page 12, line 13

$La_{2-x}Sn_xNiO_{4-y}$  at page 12, line 17

$Ce_{2-x}Cu_xNiO_{4-y}$  at page 12, line 19

$La_2CuO_4$  at page 12, line 21

$La_2CuO_{4-y}$  with  $Sn^{2x}$  substitution at page 13, line 17

$Ba^{2x}$  and  $Ca^{2x}$



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$\text{La}_{2-x}\text{Sn}_x\text{CuO}_{4-y}$  at page 17, line 21

$\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$  at page 17, line 21

$\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  at page 18, line 6

$\text{La}_2\text{CuO}_4$  :Ba at page 18, line 15

$\text{La}_2\text{CuO}_4$  :Ba at page 24, line 6

$\text{Nd}_2\text{NiO}_4$  :Sn at page 24, line 9

$\text{La}_2\text{CuO}_{4-y}$  doped with  $\text{Sn}^{2x}$ ,  $\text{Ca}^{2x}$  and  $\text{Ba}^{2x}$  at page 25, lines 6-18

The paragraph bridging pages 13 and 14 refer to Ba-La-Cu-O systems having different crystallographic phases having  $\text{Cu}^{3+}$  and  $\text{Cu}^{2+}$  ions or  $\text{Ni}^{3+}$  and  $\text{Ni}_2$  ions.

The claims under appeal In re Fisher are directed to increasing the potency of substances containing ACTH hormones for injection into human beings. In regards to the rejection for insufficient disclosure under 35 USC 112 the CCPA states that:

"the issue thus presented is whether an inventor with the first to achieve potency of greater than 1.0 for certain types of compositions, which potency was long designed because of its beneficial effects on humans, should be allowed to dominate all compositions having potencies greater than 1.0, thus including future compositions having potencies in excess

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of those obtainable from his teachings plus ordinary skill." 166 USPQ 18, 23-24 (emphasis in the original).

The CCPA goes on to say in *In re Fisher* that:

"It is apparent that such an inventor should be allowed to dominate the future patentable inventions of others where those inventions were based in some way on his teachings. Such improvements, while unobvious from his teachings, are still within his contribution, since the improvement was made possible by his work. It is equally apparent, however, that he must not be committed to achieve this dominance by claims which are insufficiently supported and hence, not in compliance with the first paragraph of 35 USC 112. That paragraph requires that the scope of the claims must bear a reasonable correlation to the scope of enablement provided by the specification to persons of ordinary skills in the art... In cases involving unpredictable factors, such as most chemical reactions... the scope of enablement obviously varies inversely with the degree of unpredictability of the factors involved." (166 USPQ 18, 24)

Applicants of the present invention have provided the first

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teaching that transition metal oxides can form a superconductor having a critical temperature in excess of 20°K, therefore, "is apparent that such an [applicant] should be allowed to dominate the future patentable inventions of others when those inventions [are based in some way on applicants] teaching" as stated by the CCPA in *In re Fisher Supra*.

Claim 103 of the present invention recites "a copper oxide compound having a layer-type-perovskite-like crystal structure, the copper oxide compound including at least one rare-earth or rare-earth-like element, and at least one alkaline-earth element". In regard to the stated elements, the rare earth elements are defined in the specification at page 7, lines 9-12 to be "a group IIIB element, such as La." Group IIIB includes Sc, Y, La and Ac, rare earth-like or near rare earth. The rare earth elements are elements 58 to 71. This group contains four elements from group IIIB and fourteen elements from the rare-earth for a total of 18 elements. The alkaline earths contain the elements of Group A which has 6 elements.

The claimed invention in *re Angstadt and Griffen* (190 USPQ 214) involves a method of catalytically oxidizing alkylaromatic hydrocarbons to form a reaction comprising the corresponding hydroperoxides. The method employs catalysts. The Examiner rejected all the claims under 35 USC 112, first and second

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paragraphs. The Board's rational for affirming the Examiner's rejection was directed primarily to the enablement required of the first paragraph.

The CCPA stated that:

"what is a maximum concern in the analysis of whether a particular claim is supported by the disclosure in an application, is whether the disclosure contains sufficient teaching regarding the subject matter of the claims as enabled one of skill in the art to make and to use the claimed invention. These two requirements 'how to make' and 'how to use' have some times been referred to in combination as the 'enablement requirement'... The relevancy may be summed up as being whether the scope of enablement provided to one of ordinary skill in the art by the disclosure as such as to be commensurate with the scope or protection sought by the claims. (190 USPQ 214,47 citing In re Moore 169 USPQ).

In the attached affidavits under 37 CFR 132, Dr. T. Dinger and Dr. D. Mitzi state:

"That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above

26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by claims 24-26, 86-90 and 96-108, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Müller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery."

In the paragraph at the bottom of page 15 of the specification, it is stated that:

in regard to compositions according to the present invention that "their manufacture generally follows the known principles of ceramic fabrication." Thereafter, an example of a typical manufacturing process is given.

The CCPA in *In re Angstadt and Griffen* further states that:

"we cannot agree with the Board that

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Appellants' disclosure is not sufficient to enable one of ordinary skill in the art to practice the invention without undo experimentation. We note that many chemical processes and catalytic processes particularly, are unpredictable, ... , and the scope of enablement varies inversely with the degree of unpredictability involved... The question, then, whether in an unpredictable art, section 112 requires the disclosure of a test with every species covered by a claim. To require such a complete disclosure will apparently necessitate a patent application or applications with 'thousands ' of examples.... More importantly, such a requirement would force an inventor to seek adequate patent protection to carry out a prohibited number of natural experiments. This would tend to discourage inventors in filing patent applications in an unpredictable area since the patent claim would have to be limited those embodiments which are expressly disclosed. A potential infringer could readily avoid 'infringement of such claims' by merely finding another analogous (example) which could be used..." 190 USPQ 124, 218.

The CCPA in *In re Angstadt* further goes on to say

"having decided that appellants are *not* required to

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disclose every *species* encompassed by the claims even in an unpredictable art such as the present record presents, each case must be determined on its own facts." 190 USPQ 214, 218. (emphasis in the original).

In regards to the catalyst In re Angstadt and Griffen CCPA further states:

"since appellants have supplied the list of catalysts and have taught how to make or how to use them, we believe that the experimentation required to determine which catalyst will produce hydroperoxide would not be undo and certainly would not 'require ingenuity beyond that to be expected of one of ordinary skill in the art'. 190 USPQ, 214, 218 in re Field v. Connover 170 USPQ, 276, 279 (1971).

As stated in the affidavits of Dr. Dinger and Dr. Mitzi, to make the high temperature superconductors encompassed by claims 24-26, 86-90 and 96-108, using the teaching of the present invention would not require ingenuity beyond that expected of one of ordinary skill in the art.

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The CCPA in In re Angstadt further states that:

"the basic policy of the Patent Act, which is to encourage disclosure of inventions and thereby to promote progress in the useful arts. To require disclosures in patent applications to transcend the level of knowledge of those skilled in the art would stifle the disclosure of inventions in fields man understands imperfectly." 190 USPQ 214, 219.

The CCPA further states that:

"the certainty which the law requires in patents is not greater than is reasonable." 242 USPQ, 270-271, cited in In re Angstadt. 190 USPQ 214, 219.

The Examiner cited In re Colianni 195 USPQ 150 which applicants believe is not on point since in In re Colianni "[t]here is not a single specific example or embodiment by way of an illustration of how the claimed method is to be practiced." (195 USPQ 150, 152). In contradistinction as noted above, there are numerous examples cited in applicants' specification and incorporated references.

"Showing that the disclosure entails undue experimentation is



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part of the PTO's initial burden." In re Armbruster 185 USPQ 152, 504.

"The practice approach followed consistently by [the CCPA] ..., places the initial burden on the PTO to show that the enabling disclosure is not commensurate in scope with the claim. Upon such a showing, the burden of rebuttal shifts to applicants". In re Coliani 195 USPQ 150.

"However, [the CCPA] has made it clear that the Patent and Trademark Office must substantiate its rejections for lack of enablement with reasons" In re Armbruster 185 USPQ 152, 153.

The Examiner has merely asserted without support that "the art of high temperature superconductivity is unpredictable...".

The CCPA in In re Marzocchi, 58 CCPA 1069, 439 F. 2d 220, 169 USPQ 367, 369-370 (1971) states:

"The only relevant concern of the Patent Office under these circumstances should be over the truth of any such assertion. The first paragraph of §112 requires nothing more than objective enablement. How such a teaching is set forth, either by the use of illustrative examples or by broad terminology, is of no importance.

As a matter of Patent Office practice, then, a specification disclosure which contains a teaching of the manner and process of making and using the invention in terms which correspond in scope to those used in describing and defining the subject matter sought to be patented *must* be taken as in compliance with the enabling requirement of the first paragraph of §112 *unless* there is reason to doubt the objective truth of the statements contained therein which must be relied on for enabling support. Assuming that sufficient reason for such doubt does exist, a rejection for failure to teach how to make and/or use will be proper on that basis; such a rejection can be overcome by suitable proofs indicating that the teaching contained in the specification is truly enabling...

[I]t is incumbent upon the Patent Office, whenever a rejection on this basis is made, to explain *why* it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement. Otherwise, there would be no need for the applicant to go to the trouble and expense of supporting his presumptively accurate

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disclosure. [Emphasis in original footnote  
deleted].

Applicants have enclosed herewith affidavits of Dr. Mitzi and Dr. Dinger under 37 CFR 132 which state, as quoted above, that once a person of skill in the art knows of applicants' work, the compositions encompassed by the claims under experimentation, can be made using the teaching of applicants without under experimentation.

Thereby rebutting the Examiner's statement that:

"[the specification ... [fails] to provide an enabling disclosure commensurate with the scope of the claims."

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Rejection of Claims 86-87 and 96-108 Under 35 USC 112, Second Paragraph

Claims 86-87 and 96-108 have been rejected under 35 USC 112, second paragraph.

The Examiner states that:

"The terms 'layer-type', 'perovskite-like',  
'earth-like' are vague and confusing."

The Examiner's attention is directed to the specification at page 7, lines 12-15 where it is stated that "substitutions can be found in the rare earth (or rare earth-like) sites, or in the transition metal sites of the compositions. A person of skill in the art would understand this to mean that a location occupied by a rare earth element can also be occupied by another element which would have chemical properties similar enough to the rare earth elements such that it would fit in to the latter site occupied by the rare earth element.

The Examiner's attention is directed to the book entitled "Copper-Oxide Superconductors", Charles P. Poole, Jr. et al., 1988, John Wiley and Sons. The Preface at page V states that "this volume reviews the experimental aspects of the field of oxide  
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superconductivity with transition temperatures between 30°K to above 120°K from the time of discovery by Bednorz and Muller in April 1986 until a few months after the award of the Nobel Prize to them, in October 1987. During this period, a consistent experimental description of many of the properties of the principal superconducting compounds, such as BiSrCaCuO, LaSrCuO, TlBaCaCuO and YBaCuO has emerged" (emphasis added)

This is clear evidence that it is generally accepted that Applicants work initiated the field of high temperature superconductivity and that the other compounds developed behave similarly. At page 78 of this book, it is stated under the heading "Perovskite-type superconducting structures" that "in their first report on high-temperature superconductors, Bednorz and Müller referred their samples as 'metallic oxygen deficient... perovskite-like mixed valent copper compounds.' Subsequent work as confirmed that the new superconductors do indeed have these characteristics. In this section, we will comment on their perovskite-like aspects." This is clear evidence that a person of skill in this art, at the time of applicants' invention, would have understood the meaning of "perovskite-like". In this book, at page 86, under the heading "'Layering Scheme of LrCuO'" it is stated that "when we describe the LrCuO structures were left out, what is perhaps their most important characteristics, their layered aspect." Therefore, it is apparent that a person of ordinary skill in the art at the time of

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applicant's invention, would have understood the meaning of "layer-like." At page 15 of this book, it is stated that "these are cases such as ... in which  $T_c$  is less composition dependent and the highest value does not occur at the stoichiometric compositions." Therefore, it is apparent that a person of ordinary skill in the art at the time the invention was made, would understand the meaning of "non-stoichiometric atomic proportion". Copies of the pages corresponding to these quoted sections is attached in Appendix D.

In re Borkowski 164 USPQ 642, 646, the CCPA states that:

[6] "we do not agree ... that claims ... are rendered "unduly broad" or "indefinite" . Moreover, there is no magical relation between the number of representative examples and the breath of the claims; the number and variety of examples are irrelevant if the disclosure is "enabling" and sets forth the "best mode contemplated".

The Examiner further states that "it should be noticed, that at the time the invention was made, the theoretical mechanism of superconductivity of these materials, was not understood. That mechanism is still not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the

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claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity". Applicants respectfully disagree. It is not necessary that applicants have a theoretical understanding of their invention. The comments herein and in particular the affidavits of Dr. Dinger and Dr. Mitzi, clearly point out that there is a factual basis for extending the scope of the claims beyond the proportions and materials actually demonstrated.

As stated in the affidavit of Dr. Mitzi and Dr. Dinger and the preface of the book by Poole et al., quoted above, the work of Applicants initiated the field of high temperature superconductors. As stated above according In re Fisher "it is apparent that such an inventor should be allowed to dominate future patentable inventions of others where those inventions were based in some way on his teachings." (166 USPQ 18, 24)

The Examiner quotes from Brenner v. Manson, 148 USPQ which states that "a patent is not a hunting license or is not a reward for the search, but a reward for a successful conclusion." Applicants respectfully disagree that this passage is applicable to applicants' situation. In Brenner v. Manson, the issue to which this quotation refers is whether an applicant may patent a chemical process which produces a product for which there is no known use. This is not the case in the above-identified application,

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therefore, the quoted passage from Brenner v. Manson is not applicable.

Claims 24-26, 86-90 and 96-108 have been rejected under 35 USC 112, first paragraph for the reasons set forth in the rejections to the specification. Claims 24-26 were originally filed in the application, are therefore supported by it since claims are self-supporting. Claims 86-90 and 96-102 are supported by the specification for the same reasons given above, for why claims 103-108 are supported by the specification.

The Examiner queries "will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?"

The claims are directed only to these materials that are superconducting. A claim which covers an inoperative species does not fail to satisfy 35 USC 112. In the present application, none of the species which the claim reads on are inoperative, since the claims only read on superconducting compositions. In *In re Angstadt*, 190 USPQ 214, 119, the CCPA held that inoperative examples do not render claims unpatentable under 35 USC 112.

We hold that the evidence as a whole, including the



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inoperative as well as the operative examples, negates the PTO position that persons of ordinary skill in *this* art, given its unpredictability, must engage in *undue* experimentation to determine which complexes work. The key word is "undue", not "experimentation". 190 USPQ 214, 719 (emphasis on the original)

Claims Rejections Under 35 USC 102

Claims 24-26, 86-90 and 96-108 have been rejected under 35 USC 102 (a) as being anticipated by Asahi Shinbum, International Satellite Edition (London, November 28, 1986). The Examiner states "as discussed in paper number 20 of the ancestral application, 07/053, 307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later than around December 13, 1986, the date samples were tested in the US to show superconductivity."

Applicants respectfully disagree.

In the Affidavit of Sung Il Park, dated March 30, 1988, at paragraph 4, it is stated "the preparation in measurement of the aforementioned superconducting samples occurred at a date prior to

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November 15, 1986, and to the best of my recollection, occurred on or about November 9, 1986, the date when a Helium dower was pumped down preparatory to taking the actual measurement." Therefore, since measurements were taken prior to the date of publication of the Asahi Shinbum article, which was November 28, 1986 the invention was reduced to practice in the US prior to the publication date of the Asahi Shinbum article.

In view of these remarks, the Examiner is respectfully requested to withdraw the rejection of claims 24-26, 86-90 and 96-108 under 35 USC 102(a) as being anticipated by the Asahi Shinbum article.

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Claim Rejection - 35 USC 103

Claims 24-26, 86-90 and 96-108 have been rejection under 35 USC 103 as being unpatentable over Asahi Shinbum article. For the reasons given above in response to the rejection of these claims under 35 USC 102 as anticipated by the Ashahi Shinbum article, that article cannot be considered a reference, therefore, these claims cannot be obvious in view thereof.

In view of these remarks, the Examiner is respectfully requested to withdraw the rejection of claims 24-26, 86-90 and 96-108 under 35 USC 103 as being unpatentable over the Asahi Shinbum article.

The Examiner is respectfully requested to consider this application in view of these remarks and the changes made to the claims. If the Examiner wishes to discuss the application further, or if additional information would be required, the undersigned will cooperate fully to assist in the prosecution of this application.

Respectfully submitted,

A handwritten signature in cursive script, appearing to read "Daniel P. Morris".

By: Daniel P. Morris  
Registration No. 32,043

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# Appendix A

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New superconductive compounds of the K<sub>2</sub>NiF<sub>4</sub> structural type having a high transition temperature, and method for fabricating same.

The superconductive compounds are oxides of the general formula RE<sub>2-x</sub>AE<sub>x</sub>TM.O<sub>4-y</sub>, wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two member of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ . The method for making these compounds involves the steps of coprecipitating aqueous solutions of the respective nitrates of the constituents and adding the coprecipitate to oxalic acid, decomposing the precipitate and causing a solid-state reaction at a temperature between 500 and 1200°C for between one and eight hours, forming pellets of the powdered product at high pressure, sintering the pellets at a temperature between 500 and 1000°C for between one half and three hours, and subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for between one half and five hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product.

EP 0 275 343 A1

# NEW SUPERCONDUCTIVE COMPOUNDS OF THE $K_2NiF_4$ STRUCTURAL TYPE HAVING A HIGH TRANSITION TEMPERATURE, AND METHOD FOR FABRICATING SAME

## Field of the Invention

The invention relates to a new class of superconductors, in particular to components of the  $K_2NiF_4$  type of structure having superconductor properties below a relatively high transition temperature, and to a method for manufacturing those compounds.

## Background of the Invention

Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials: About a quarter of the elements and over 1000 alloys and compounds have been found to be superconductors. Superconductivity is considered a property of the metallic state of the material, in that all known superconductors are metallic under the conditions that cause them to superconduct. A few normally non-metallic materials, for example, become superconductive under very high pressure, the pressure converting them to metals before they become superconductors.

Superconductors are very attractive for the generation and energy-saving transport of electrical power over long distances, as materials for forming the coils of strong magnets for use in plasma and nuclear physics, in nuclear resonance medical diagnosis, and in connection with the magnetic levitation of fast trains. Power generation by thermonuclear fusion, for example, will require very large magnetic fields which can only be provided by superconducting magnets. Certainly, superconductors will also find application in computers and high-speed signal processing and data communication.

While the advantages of superconductors are quite obvious, the common disadvantage of all superconductive materials so far known lies in their very low transition temperature (usually called the critical temperature  $T_c$ ) which is typically on the order of a few degrees Kelvin. The element with the highest  $T_c$  is niobium (9.2 K), and the highest known  $T_c$  is about 23 K for  $Nb_3Ge$  at ambient pressure.

Accordingly, most known superconductors require liquid helium for cooling and this, in turn, requires an elaborate technology and as a matter of principle involves a considerable investment in cost and energy.

It is, therefore, an object of the present inven-

tion to propose compositions for high- $T_c$  superconductors and a manufacturing method for producing compounds which exhibit such a high critical temperature that cooling with liquid helium is obviated so as to considerably reduce the cost involved and to save energy.

The present invention proposes to use compounds having a layer-type structure of the kind known from potassium nickel fluoride  $K_2NiF_4$ . This structure is in particular present in oxides of the general composition  $RE_2TM.O_x$ , wherein RE stands for the rare earths (lanthanides) and TM stands for the so-called transition metals. It is a characteristic of the present invention that in the compounds in question the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group, and that the oxygen content is at a deficit.

For example, one such compound that meets the description given above is lanthanum copper oxide  $La_2CuO_4$  in which the lanthanum -which belongs to the IIIB group of elements- is in part substituted by one member of the neighboring IIA group of elements, viz. by one of the alkaline earth metals (or by a combination of the members of the IIA group), e.g., by barium. Also, the oxygen content of the compound is incomplete such that the compound will have the general composition  $La_{2-x}Ba_xCuO_{4-y}$ , wherein  $x \leq 0.3$  and  $y < 0.5$ .

Another example for a compound meeting the general formula given above is lanthanum nickel oxide wherein the lanthanum is partially substituted by strontium, yielding the general formula  $La_{2-x}Sr_xNiO_{4-y}$ . Still another example is cerium nickel oxide wherein the cerium is partially substituted by calcium, resulting in  $Ce_{2-x}Ca_xNiO_{4-y}$ .

The following description will mainly refer to barium as a partial replacement for the lanthanum in a  $La_2CuO_4$  compound because it is the Ba-La-Cu-O system which is, at least at present, the best understood system of all possible. Some compounds of the Ba-La-Cu-O system have been described by C. Michel and B. Raveau in Rev. Chim. Min. 21 (1984) 407, and by C. Michel, L. Er-Rakho and B. Raveau in Mat. Res. Bull., Vol. 20, (1985) 687-671. They did, however, not find nor try to find, superconductivity.

Experiments conducted in connection with the present invention have revealed that high- $T_c$  superconductivity is present in compounds where the rare earth is partially replaced by any one or more of the other members of the same IIA group of elements, i.e. the other alkaline earth metals. Ac-

tually, the  $T_c$  of  $\text{La}_2\text{CuO}_{4-y}$  with  $\text{Sr}^{2+}$  is higher and is superconductivity-induced diamagnetism larger than that found with  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ .

As a matter of fact, only a small number of oxides is known to exhibit superconductivity, among them the Li-Ti-O system with onsets of superconductivity as high as 13.7 K, as reported by D.C. Johnston, H. Prakash, W.H. Zachariasen and R. Visvanathan in *Mat. Res. Bull.* 8 (1973) 777. Other known superconductive oxides include Nb-doped  $\text{SrTiO}_3$  and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , reported respectively by A. Baratoff and G. Binnig in *Physics* 108B (1981) 1335, and by A.W. Sleight, J.L. Gillson and F.E. Bierstedt in *Solid State Commun.* 17 (1975) 27.

The X-ray analysis conducted by Johnston et al. revealed the presence in their Li-Ti-O system of three different crystallographic phases, one of them, with a spinel structure, showing the high critical temperature. The Ba-La-Cu-O system, too, exhibits a number of crystallographic phases, namely with mixed-valent copper constituents which have itinerant electronic states between non-Jahn-Teller  $\text{Cu}^{2+}$  and Jahn-Teller  $\text{Cu}^{3+}$  ions.

This applies likewise to systems where nickel is used in place of copper, with  $\text{Ni}^{3+}$  being the Jahn-Teller constituent, and  $\text{Ni}^{2+}$  being the non-Jahn-Teller constituent.

The existence of Jahn-Teller polarons in conducting crystals was postulated theoretically by K.H. Hoeck, H. Nickisch and H. Thomas in *Helv. Phys. Acta* 56 (1983) 237. Polarons have large electron-phonon interactions and, therefore, are favorable to the occurrence of superconductivity at high critical temperatures.

Generally, the Ba-La-Cu-O system, when subjected to X-ray analysis reveals three individual crystallographic phases, viz.

- a first layer-type perovskite-like phase, related to the  $\text{K}_2\text{NiF}_6$  structure, with the general composition  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ , with  $x < 1$  and  $y \geq 0$ ;
- a second, non-conducting CuO phase; and
- a third, nearly cubic perovskite phase of the general composition  $\text{La}_{1-x}\text{Ba}_x\text{CuO}_{3-y}$ , which appears to be independent of the exact starting composition,

as has been reported in the paper by J.G. Bednorz and K.A. Müller in *Z. Phys. B - Condensed Matter* 64 (1986) 189-193. Of these three phases the first one appears to be responsible for the high- $T_c$  superconductivity, the critical temperature showing a dependence on the barium concentration in that phase. Obviously, the  $\text{Ba}^{2+}$  substitution causes a mixed-valent state of  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  to preserve charge neutrality. It is assumed that the oxygen deficiency,  $y$ , is the same in the doped and undoped crystallites.

Both  $\text{La}_2\text{CuO}_4$  and  $\text{LaCuO}_3$  are metallic conduc-

tors at high temperatures in the absence of barium. Actually, both are metals like  $\text{LaNiO}_3$ . Despite their metallic character, the Ba-La-Cu-O type materials are ceramics, as are the other compounds of the  $\text{RE}_2\text{TM}_2\text{O}_7$  type, and their manufacture more or less follows the known principles of ceramic fabrication. The preparation of a Ba-La-Cu-O compound, for example, in accordance with the present invention typically involves the following manufacturing steps:

- Preparing aqueous solutions of the respective nitrates of barium, lanthanum and copper and coprecipitation thereof in their appropriate ratios.
- Adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates.
- Decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for one to eight hours.
- Pressing the resulting product at a pressure of about 4 kbar to form pellets.
- Re-heating the pellets to a temperature between 500 and 900°C for one half to three hours for sintering.

It will be evident to those skilled in the art that if the partial substitution of the lanthanum by strontium or calcium is desired, the particular nitrate thereof will have to be used in place of the barium nitrate of the example described above. Also, if the copper of this example is to be replaced by another transition metal, the nitrate thereof will obviously have to be employed.

Experiments have shown that the partial contents of the individual compounds in the starting composition play an important role in the formation of the phases present in the final product. While, as mentioned above, the final Ba-La-Cu-O system obtained generally contains the said three phases, with the second phase being present only to a very small amount, the partial substitution of lanthanum by strontium or calcium (and perhaps beryllium) will result in only one phase existing in the final  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  or  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$ , respectively, provided  $x < 0.3$ .

With a ratio of 1:1 for the respective (Ba, La) and Cu contents, one may expect the said three phases to occur in the final product. Setting aside the said second phase, i.e. the CuO phase, whose amount is negligible, the relative volume amounts of the other two phases are dependent on the barium contents in the  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  complex. At the 1:1 ratio and with an  $x = 0.02$ , the onset of a localization transition is observed, i.e., the resistivity increases with decreasing temperature, and there is no superconductivity.

With  $x = 0.1$  at the same 1:1 ratio, there is a resistivity drop at the very high critical temperature of 35 K.



With a (Ba,La) versus Cu ratio of 2:1 in the starting composition, the composition of the  $\text{La}_2\text{CuO}_4\text{Ba}$  phase, which was assumed to be responsible for the superconductivity, is limited, with the result that now only two phases are present, the CuO phase not existing. With a barium content of  $x = 0.15$ , the resistivity drop occurs at  $T_c = 26$  K.

The method for preparing the Ba-La-Cu-O complex involves two heat treatments for the precipitate at an elevated temperature for several hours. In the experiments carried out in connection with the present invention it was found that best results were obtained at  $900^\circ\text{C}$  for a decomposition and reaction period of 5 hours, and again at  $900^\circ\text{C}$  for a sintering period of one hour. These values apply to a ratio 1:1 composition as well as to a 2:1 composition.

For the ratio 2:1 composition, a somewhat higher temperature is permissible owing to the melting point of the composition being higher in the absence of excess copper oxide. Yet it is not possible by high-temperature treatment to obtain a one-phase compound.

Measurements of the dc conductivity were conducted between 300 and 4.2 K. For barium-doped samples, for example, with  $x < 0.3$ , at current densities of  $0.5 \text{ A/cm}^2$ , a high-temperature metallic behavior with an increase in resistivity at low temperatures was found. At still lower temperatures, a sharp drop in resistivity ( $>90\%$ ) occurred which for higher current densities became partially suppressed. This characteristic drop was studied as a function of the annealing conditions, i.e. temperature and oxygen partial pressure. For samples annealed in air, the transition from itinerant to localized behavior was not found to be very pronounced, annealing in a slightly reducing atmosphere, however, led to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop was shifted towards higher values of the critical temperature. Longer annealing times, however, completely destroy the superconductivity.

Cooling the samples from room temperature, the resistivity data first show a metal-like decrease. At low temperatures, a change to an increase occurs in the case of Ca compounds and for the Ba-substituted samples. This increase is followed by a resistivity drop, showing the onset of superconductivity at  $22 \pm 2$  K and  $33 \pm 2$  K for the Ca and Ba compounds, respectively. In the Sr compound, the resistivity remains metallic down to the resistivity drop at  $40 \pm 1$  K. The presence of localization effects, however, depends strongly on alkaline-earth ion concentration and sample preparation, that is to say, annealing conditions and also on the density which have to be optimized. All samples with low

concentrations of Ca, Sr, and Ba show a strong tendency to localization before the resistivity drop occurs.

Apparently, the onset of the superconductivity, i.e. the value of the critical temperature  $T_c$ , is dependent, among other parameters, on the oxygen content of the final compound. It seems that a certain oxygen deficiency is necessary for the material to have a high- $T_c$  behavior. In accordance with the present invention, the method described above for making the  $\text{La}_2\text{CuO}_4\text{Ba}$  complex is complemented by an annealing step during which the oxygen content of the final product can be adjusted. Of course, what was said in connection with the formation of the  $\text{La}_2\text{CuO}_4\text{Ba}$  compound, likewise applies to other compounds of the general formula  $\text{RE}_2\text{TM}_2\text{O}_4\text{AE}$ , such as, e.g.  $\text{Nd}_2\text{NiO}_4\text{Sr}$ .

In the cases where a heat treatment for decomposition and/or reaction for sintering was performed at a relatively low temperature, i.e. at no more than  $950^\circ\text{C}$ , the final product is subjected to an annealing step at about  $900^\circ\text{C}$  for about one hour in a reducing atmosphere. It is assumed that the net effect of this annealing step is a removal of oxygen atoms from certain locations in the matrix of the  $\text{RE}_2\text{TM}_2\text{O}_4$  complex, thus creating a distortion in its crystalline structure. The  $\text{O}_2$  partial pressure for annealing in this case may be between  $10^{-1}$  and  $10^{-5}$  bar.

In those cases where a relatively high temperature (i.e. above  $950^\circ\text{C}$ ) was employed for the heat treatment, it might be advantageous to perform the annealing step in a slightly oxidizing atmosphere. This would make up for an assumed exaggerated removal of oxygen atoms from the system owing to the high temperature and resulting in a too severe distortion of the system's crystalline structure.

Resistivity and susceptibility measurements, as a function of temperature, of  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ -doped  $\text{La}_2\text{CuO}_{4-x}$  ceramics show the same general tendency as the  $\text{Ba}^{2+}$ -doped samples: A drop in resistivity  $\rho(T)$ , and a crossover to diamagnetism at a slightly lower temperature. The samples containing  $\text{Sr}^{2+}$  actually yielded a higher onset than those containing  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ . Furthermore, the diamagnetic susceptibility is about three times as large as for the Ba samples. As the ionic radius of  $\text{Sr}^{2+}$  nearly matches the one of  $\text{La}^{3+}$ , it seems that the size effect does not cause the occurrence of superconductivity. On the contrary, it is rather adverse, as the data on  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  indicate.

The highest  $T_c$ 's for each of the dopant ions investigated occur for those concentrations where, at room temperature, the  $\text{Re}_{2-x}\text{TM}_2\text{O}_{4-x}$  structure is close to the orthorhombic-tetragonal structural phase transition which may be related to the substantial electron-phonon interaction enhanced by the substitution. The alkaline-earth substitution of

the rare earth metal is clearly important, and quite likely creates TM ions with no  $e_g$  Jahn-Teller orbitals. Therefore, the absence of these J.-T. orbitals, that is, J.-T. holes near the Fermi energy probably plays an important role for the  $T_c$  enhancement.

#### Claims

1) Superconductive compound of the  $RE_2TM.O_4$  type having a transition temperature above 28 K, wherein the rare earth (RE) is partially substituted by one or more members of the alkaline earth groups of elements (AE), and wherein the oxygen content is adjusted such that the resulting crystal structure is distorted and comprises a phase of the general composition  $RE_{2-x}AE_yTM.O_{4-y}$ , wherein TM represents a transition metal, and  $x < 0.3$  and  $y < 0.5$ .

2) Compound in accordance with claim 1, wherein the rare earth (RE) is lanthanum and the transition metal (TM) is copper.

3) Compound in accordance with claim 1, wherein the rare earth is cerium and the transition metal is nickel.

4) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is nickel.

5) Compound in accordance with claim 1, wherein barium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

6) Compound in accordance with claim 1, wherein calcium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

7) Compound in accordance with claim 1, wherein strontium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

8) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is chromium.

9) Compound in accordance with claim 1, wherein the rare earth is neodymium and the transition metal is copper.

10) Method for making superconductive compounds of the  $RE_2TM.O_4$  type, with RE being a rare earth, TM being a transition metal, the compounds having a transition temperature above 28 K, comprising the steps of:

- preparing aqueous solutions of the nitrates of the rare earth and transition metal constituents and of one or more of the alkaline earth metals and coprecipitation thereof in their appropriate ratios;
- adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates;
- decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for a period of

time between one and eight hours;

- allowing the resultant powder product to cool;
- pressing the powder at a pressure of between 2 and 10 kbar to form pellets;
- re-adjusting the temperature of the pellets to a value between 500 and 1000°C for a period of time between one half and three hours for sintering;
- subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for a period of time between one half and 5 hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product which has a final composition of the form  $RE_{2-x}TM.O_{4-y}$ , wherein  $x < 0.3$  and  $0.1 < y < 0.5$ .

11) Method in accordance with claim 10, wherein the protected atmosphere is pure oxygen.

12) Method in accordance with claim 10, wherein the protected atmosphere is a reducing atmosphere with an oxygen partial pressure between  $10^{-1}$  and  $10^{-3}$  bar.

13) Method in accordance with claim 10, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed at a temperature of 900°C for one hour in a reducing atmosphere with an oxygen partial pressure between  $10^{-1}$  and  $10^{-3}$  bar.

14) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

15) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

16) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein calcium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

17) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein strontium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

18) Method in accordance with claim 10, wherein cerium is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the cerium, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

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Office

# EUROPEAN SEARCH REPORT

Application number

EP 87 10 0961

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |  |  |
|---|--|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| D, A  | REVUE DE CHIMIE MINERALE, vol. 21, 1984, pages 407-425, Paris, FR; C. MICHEL et al.: "Oxygen intercalation in mixed valence copper oxides related to the perovskites"<br>* page 417, paragraph 2 - page 425 *<br><br>----- | 1  | H 01 L 39/12                                   |
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| <b>CATEGORY OF CITED DOCUMENTS</b>  |  |  |  |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br><br>& : member of the same patent family, corresponding document |  |

## Appendix B

# *Solid State Physics*

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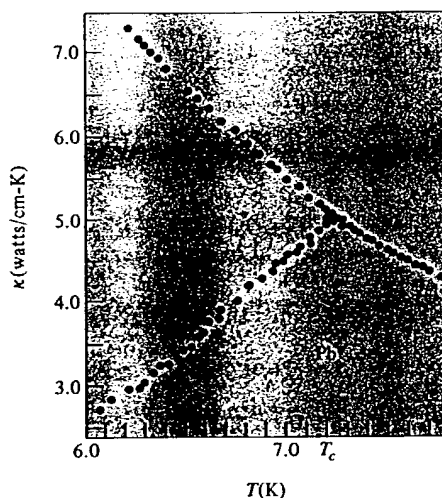
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Figure 34.2

The thermal conductivity of lead. Below  $T_c$  the lower curve gives the thermal conductivity in the superconducting state, and the upper curve, in the normal state. The normal sample is produced below  $T_c$  by application of a magnetic field, which is assumed otherwise to have no appreciable effect on the thermal conductivity. (Reproduced by permission of the National Research Council of Canada from J. H. P. Watson and G. M. Graham, *Can. J. Phys.* 41, 1738 (1963).)



conductivity indicates that even when a superconductor is not carrying an electric current, only a fraction of its conduction electrons are capable of transporting entropy.<sup>15</sup>

### MAGNETIC PROPERTIES: PERFECT DIAMAGNETISM

A magnetic field (provided that it is not too strong) cannot penetrate into the interior of a superconductor. This is most dramatically illustrated by the Meissner-Ochsenfeld effect: If a normal metal in a magnetic field<sup>16</sup> is cooled below its superconducting transition temperature, the magnetic flux is abruptly expelled. Thus the transition, when it occurs in a magnetic field, is accompanied by the appearance of whatever surface currents are required to cancel the magnetic field in the interior of the specimen.

Note that this is not implied by perfect conductivity (i.e.,  $\sigma = \infty$ ) alone, even though perfect conductivity does imply a somewhat related property: If a perfect conductor, initially in zero magnetic field, is moved into a region of nonzero field (or if a field is turned on), then Faraday's law of induction gives rise to eddy currents that cancel the magnetic field in the interior. If, however, a magnetic field were established in a perfect conductor, its expulsion would be equally resisted. Eddy currents would be induced to maintain the field if the sample were moved into a field-free region (or if the applied field were turned off). Thus perfect conductivity implies a time-independent magnetic field in the interior, but is noncommittal as to the value that field must have. In a superconductor, the field is not only independent of time, but also zero.

<sup>15</sup> Presumably the efficacy of the phonons in conducting heat remains undiminished, but this is generally a less important contribution to the thermal conductivity than that of the conduction electrons.

<sup>16</sup> A normal metal is only weakly paramagnetic or diamagnetic (no magnetically ordered metals are superconductors) and an applied magnetic field can penetrate it.



Appendix C

# **THEORY OF SUPERCONDUCTIVITY**

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## CHAPTER 1

### Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.<sup>1</sup> He was the first to liquefy helium and so to produce temperatures below  $10^{\circ}$  K. With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about  $4.2^{\circ}$  K (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g.; gold and bismuth, the conductivity remains normal far below even  $1^{\circ}$  K. Many alloys and compounds can also become superconducting, in particular the frequently used niobium nitride which has a transition temperature as high as  $20^{\circ}$  K. However, among these latter substances hysteresis phenomena mentioned in the "Introduction" are so much more strongly evident that in testing the present theory we prefer to employ only the "good" superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at a transition temperature  $T_c$ . Actually the resistance-temperature curve does fall more sharply the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

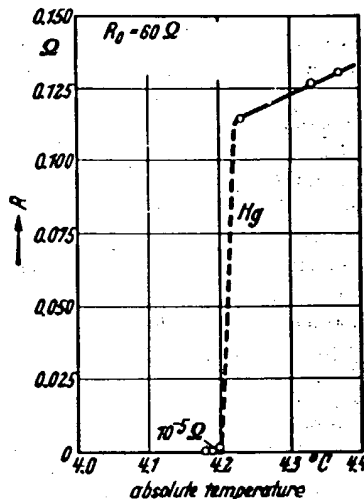


Fig. 1-1. Appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911). The ordinate is the resistance  $R$ ;  $R_0$ , the resistance of solid mercury extrapolated to  $0^{\circ}$  C, is 60 ohms.

<sup>1</sup>H. Kamerlingh-Onnes, *Commun. Leiden*, 120b, 122b, 124c, (1911).

Appendix D

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# COPPER OXIDE SUPERCONDUCTORS

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**Timir Datta**  
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*with help from*

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## PREFACE

The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. The time is now ripe to bring together in one place the results of this research effort so that scientists working in this field can better acquire an overall perspective, and at the same time have available in one place a collection of detailed experimental data. This volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 120 K, from the time of its discovery by Bednorz and Müller in April 1986 until a few months after the award of the Nobel Prize to them in October 1987. During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as  $\text{BiSrCaCuO}$ ,  $\text{LaSrCuO}$ ,  $\text{TlBaCaCuO}$ , and  $\text{YBaCuO}$  has emerged. At the same time there has been a continual debate on the extent to which the BCS theory and the electron-phonon interaction mechanism apply to the new materials, and new theoretical models are periodically proposed. We discuss these matters and, when appropriate, make comparisons with transition metal and other previously known superconductors. Many of the experimental results are summarized in figures and tables.

The field of high-temperature superconductivity is still evolving, and some ideas and explanations may be changed by the time these notes appear in print. Nevertheless, it is helpful to discuss them here to give insights into work now in progress, to give coherence to the present work, and to provide guidance for future work. It is hoped that in the not too distant future the field will settle down enough to permit a more definitive monograph to be written.

Fig. II-1. Periodic table showing the elements  $T_c$  are superconducting in thin films, under pressure, or after irradiation are so indicated. Re  $T_c$  in the upper right corner of the box and from top to bottom the Debye temperature  $\theta_D$ , the electronic specific heat factor  $\gamma$ , the electron-phonon coupling constant  $\lambda$ , and the density of states  $N(E_F)$  at the Fermi level. This format and the units used are shown. The number  $N_e$  of (valence) electrons outside of closed shells, 1-12, is shown for each column under the main body of the table. The Sn data are for white tin.

in the bulk state, and also some that only become superconducting in thin films, under pressure, or after irradiation. This figure gives the transition temperature  $T_c$ , the Debye temperature  $\theta_D$ , the Sommerfeld constant or normal state electronic specific heat constant  $\gamma$  from the expression  $C_n = \gamma T$ , the electron-phonon coupling constant  $\lambda$  (cf. Section IV-B-1), and the density of states  $N(E_F)$  at the Fermi level (cf. Sections IV-G and IX-C) for the various superconductors. The columns of the periodic table are labeled with the number of (valence) electrons  $N_e$  outside of closed shells. Table II-1 lists various properties of some of the transition elements. Figure II-2, which illustrates how  $T_c$  depends on  $N_e$ , has two peaks, one near  $N_e = 5$  and the other near  $N_e = 7$  (Matt2). Graphs of the specific heat constant  $\gamma$ , the magnetic susceptibility  $\chi = M/B$  and the inverse Debye temperature squared  $1/\theta_D^2$  exhibit the same dependence on  $N_e$ , with the  $N_e = 7$  peak somewhat suppressed in the Debye case (Glads, Vonso).

Among the elements niobium has the highest transition temperature, and perhaps not coincidentally it also is a constituent of higher  $T_c$  compounds like  $Nb_3Ge$ . Niobium has not appeared prominently in the newer oxide superconductors.

Of the transition elements most commonly found in the newer ceramic type superconductors lanthanum is superconducting with a moderately high  $T_c$  (4.88 K for the  $\alpha$  or fcc form and 6.3 for the  $\beta$  or hcp form), yttrium becomes superconducting only under pressure ( $T_c \approx 2$  K for  $110 \leq P \leq 160$  kbar) and copper is not known to superconduct. Studies of the transition temperature of copper alloys as a function of the copper content have provided an extrapolated value of  $T_c = 6 \times 10^{-10}$  K for Cu, which is extremely low. The nontransition elements oxygen and strontium in these compounds do not superconduct, barium only does so under pressure ( $T_c = 1-5.4$  K for pressures from 55 to 190 kbar), bismuth likewise superconducts only under pressure, and thallium is a superconductor with  $T_c = 2.4$  K. Thus the superconducting properties of the elements are not always indicative of the properties of their compounds, although niobium seems to be an exception, as was mentioned above.

## C. ALLOYS AND COMPOUNDS

Transition elements combine with a number of other elements to form superconducting materials that sometimes have higher transition temperatures than any of their constituents. These materials may be classified into alloys with the subdivisions solid solutions (with random atomic ordering) and intermetallic compounds or intermetallides (ordered crystallographically), and chemical compounds with the subdivisions ordinary compounds, semiconductors, layered compounds, and polymers. The intermetallides and ordinary compounds provide the highest transition temperatures, with solid solutions and layered compounds also moderately high.

These materials tend to be stoichiometric, and  $T_c$  is often sensitive to it. For example, the gradual approach of  $Nb_3Ge$  to stoichiometry raised its measured  $T_c$



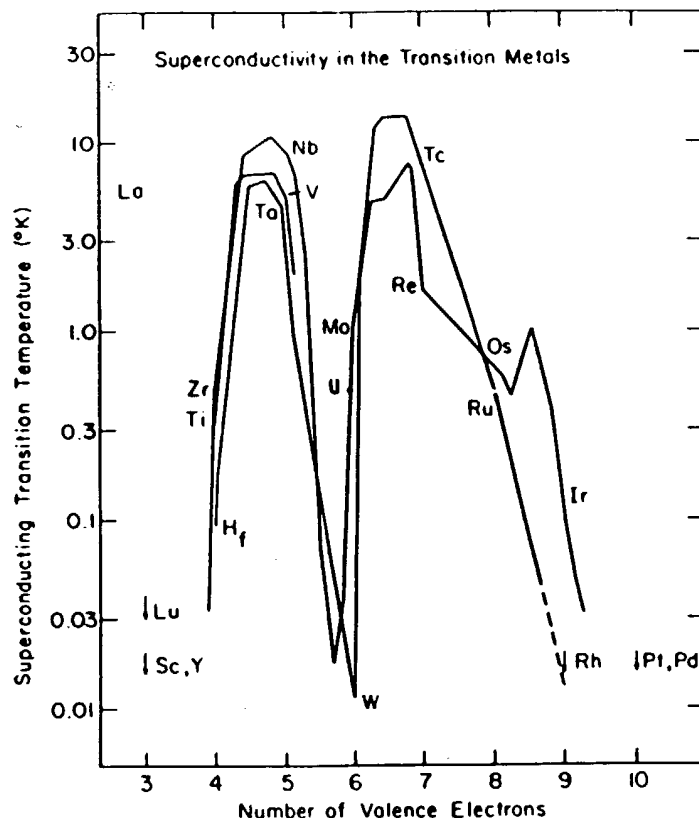


Fig. II-2. The dependence of  $T_c$  on the number of valence electrons  $N_v$  in elements and solid solutions formed by neighboring transition metals. (From Glads, p. 736; see also Hamil and Vonso, pp. 184, 239.)

from 6 to 17 K and finally to 23.2 K. In contrast, there are cases such as  $\text{Cr}_3\text{Os}$ ,  $\text{Cr}_3\text{Ir}$ ,  $\text{Mo}_3\text{Ir}$ ,  $\text{Mo}_3\text{Pt}$ , and  $\text{V}_3\text{Ir}$  in which  $T_c$  is less composition dependent and the highest value does not occur at the stoichiometric composition. This latter case is quite common among the newer superconductors.

Systematic studies of mixed alloys of neighboring transition elements produce a graph similar to Fig. II-2 with intermediate points filled in and the same two maxima. Matthias interpreted these results in terms of the presence of favorable and unfavorable regions of  $N_v$  (Matt1). Amorphous alloys only exhibit one maximum for each series. Other properties such as the electronic specific heat factor  $\gamma$ , the magnetic susceptibility  $\chi$ , the Debye temperature  $\theta_D$ , and the electron-phonon coupling constant  $\lambda$  have dependencies on electron concentration quite similar to the  $T_c$  versus  $N_v$  graph of Fig. II-2.

The highest transition temperatures of the older superconductors were ob-

tetragonal phase, and the metal-to-insulator transition occurs at the tetragonal-to-orthorhombic phase boundary  $x \approx 0.35$  (Matt7, Sleil).

#### D. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller referred to their samples as "metallic, oxygen deficient . . . perovskite like mixed valent copper compounds." Subsequent work has confirmed that the new superconductors do indeed have these characteristics. In this section we will comment on their perovskite-like aspects.

##### 1. Atom Sizes

In the oxide superconductors Cu replaces the  $Ti^{4+}$  ions ( $0.68 \text{ \AA}$ ) of perovskite, and in most cases retains the  $CuO_2$  layering with two oxygens per copper in the layer. Other cationic replacements tend to be Bi, Ca, La, Sr, Tl, and Y for the larger Ba, forming "layers" containing only one oxygen or none per cation. We see from the following list of ionic radii

|           |                    |        |
|-----------|--------------------|--------|
| $Cu^{2+}$ | $0.72 \text{ \AA}$ |        |
| $Bi^{5+}$ | $0.74 \text{ \AA}$ |        |
| $Y^{3+}$  | $0.94 \text{ \AA}$ |        |
| $Tl^{3+}$ | $0.95 \text{ \AA}$ |        |
| $Bi^{3+}$ | $0.96 \text{ \AA}$ |        |
| $Ca^{2+}$ | $0.99 \text{ \AA}$ | (VI-4) |
| $Sr^{2+}$ | $1.12 \text{ \AA}$ |        |
| $La^{3+}$ | $1.14 \text{ \AA}$ |        |
| $Ba^{2+}$ | $1.34 \text{ \AA}$ |        |
| $O^{2-}$  | $1.32 \text{ \AA}$ |        |

that there are four size groups, with all other cations significantly smaller than the Ba of perovskite. The common feature of  $CuO_2$  layers that are planar or close to planar establishes a fairly uniform lattice size in the  $a, b$  plane. The parameters of the compounds  $LaSrCuO$  ( $a = b = 3.77 \text{ \AA}$ ),  $YBaCuO$  ( $a = 3.83 \text{ \AA}$ ,  $b = 3.89 \text{ \AA}$ ),  $BiSrCaCuO$  ( $a = b = 3.82 \text{ \AA}$ ), and  $TlBaCaCuO$  ( $a = b = 3.86 \text{ \AA}$ ) are all between the ideal fcc oxygen lattice value of  $3.73 \text{ \AA}$  and the perovskite one of  $4.01 \text{ \AA}$ .

Table VI-2 gives the ionic radii of the positively charged ions of various elements of the periodic table. These radii are useful for estimating changes in lattice constant when ionic substitutions are made in existing structures. They also provide some insight into which types of substitutions will be most favorable.

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bic, superconducting, and spin-density wave (SDW) regions for the barium compound (Fujit), and data points for the strontium compound (Moret, More8). An alternate phase diagram has been proposed (Ahar1). Alkaline metal contents much larger than those shown on the figure (e.g.,  $x \approx 0.5$ ) can be non-superconducting. The SDW region occurs below the minimum concentration for the onset of superconductivity. Another work (Geise) showed that  $\text{LaSr}(0.04)$  undergoes a structural phase transition between 180 and 300 K.

### 5. Generation of $\text{LaSrCuO}$ Structures

The  $\text{LaSrCuO}$  tetragonal structures may be visualized as being derived from four  $\text{LaCuO}_3$  perovskite unit cells of the type illustrated in Fig. VI-1 stacked one above the other along the  $z$  or  $c$  axis. To generate  $\text{La}_2\text{CuO}_4$  in the  $\text{K}_2\text{NiF}_4$  structure the layers of  $\text{CuO}_2$  atoms on the  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$  levels of this four-cell stacking are removed, La and O are interchanged on two other layers, and the middle layer Cu atom is shifted from the edge to the center point  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  of the unit cell. Then the cell is compressed vertically from 14.9 to 13.2 Å (Table VI-4) to take up the space formerly occupied by the removed  $\text{CuO}_2$  layers. Finally, the lanthanums along the  $c$  axis and the oxygens along the side edges are shifted vertically to accommodate the new atom arrangement.

To generate  $\text{La}_2\text{CuO}_4$  with the  $\text{Nd}_2\text{CuO}_4$  arrangement from this same four-cell stacking all of the oxygens on the vertical edges are removed, and two lanthanums are moved to edge sites. Copper is handled the same way as before, so in both cases the generated structure lacks two  $\text{CuO}_2$  layers.

### 6. Layering Scheme of $\text{LaSrCuO}$

When we described the  $\text{LaSrCuO}$  structures we left out what is perhaps their most important characteristic, namely, their layered aspect. Lanthanum copper oxide may be looked upon as consisting of Cu-O layers of square-planar coordinated copper ions with lanthanum and O(2)-type oxygen ions populating the spaces between the layers. These Cu-O layers are stacked equally spaced, perpendicular to the  $c$  axis, as shown in Fig. VI-7, and their oxygens are aligned along the  $c$  axis, as indicated by the vertical dotted line on the left side of the figure. The copper ions, on the other hand, are not aligned vertically, but rather alternate between (000) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  sites in adjacent layers, as illustrated in Figs. VI-5 and VI-7.

The copper is actually octahedrally coordinated with oxygen, but the Cu-O distance of 1.9 Å in the  $\text{CuO}_2$  planes is much less than the vertical distance of 2.4 Å between copper and the oxygens above and below, as shown in Fig. VI-8. When the structure is distorted orthorhombically the Cu-O spacings in both the planes and the  $c$  direction remain quite close to their tetragonal counterparts.

The copper ions and the O(1)-type oxygens in the planes are both in special sites in the tetragonal and orthorhombic forms, in accordance with Eqs. (VI-6) and (VI-9), and as a result the plane is perfectly flat in both cases. When the

for the barium compound (Moret, 1981). Alkaline metal (0.5) can be non-concentration for that LaSr(0.04)  $\leq$ .

derived from four  $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$  stacked one the  $K_2NiF_4$  structure of this four-cell layers, and the unit  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  of the  $2 \text{ \AA}$  (Table VI-4) layers. Finally, the edges are shifted

this same four-cell structure, and two lanthanum as before, so

is perhaps their orthorhombic copper re-planar coordination populating the fully spaced, perpendicular layers are aligned on the left side of the figure, but rather illustrated in Figs.

on, but the Cu-O critical distance of own in Fig. VI-8. The layers in both the orthorhombic counterparts. The layers are both in special cases. When the

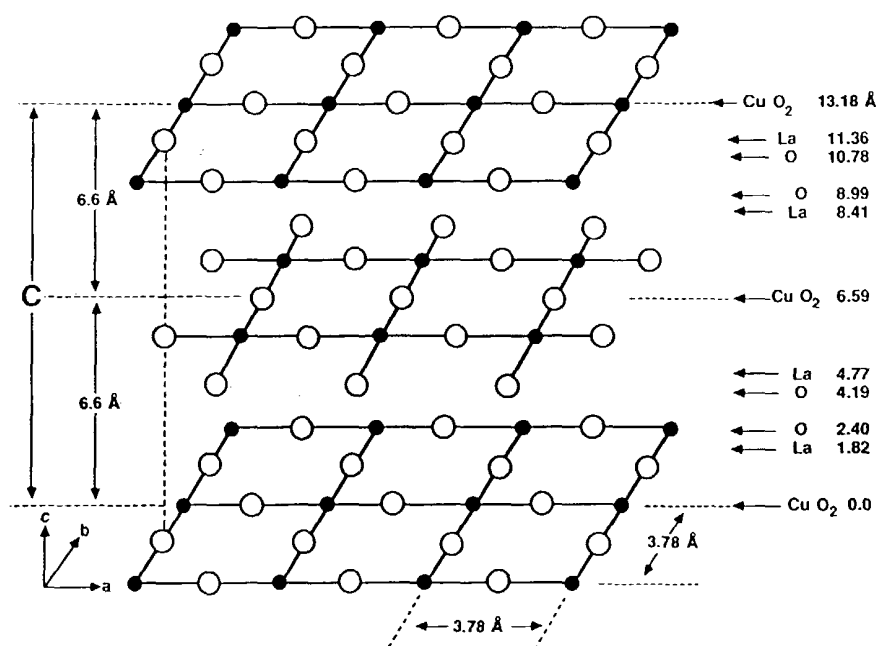


Fig. VI-7. Layering scheme of the LaSrCuO superconducting structure. The layers are perpendicular to the c axis.

structure is tetragonal the square-planar arrangement is also perfect, and of course the planes are perfectly parallel to each other. These characteristics of the planes could influence the superconducting properties.

The copper-oxygen planes are bound together by Cu-O and La-O bonds, as indicated on Fig. VI-5, and Fig. VI-8 shows the spacial arrangement of the CuO<sub>6</sub> octahedra. This figure also makes clear how the copper ions alternate along the c axis. The superconducting properties are probably less influenced by the way the planes are bound together than by the internal characteristics of the planes themselves.

## F. YTTRIUM-BARIUM-COPPER OXIDE

The YBaCuO compounds such as  $Y_{1-x}Ba_xCu_3O_{7-\delta}$ , like their LaSrCuO counterparts, come in tetragonal and orthorhombic varieties, and both will be described in turn. Then we will show how to generate the structures from their perovskite prototypes, we will explain the layering scheme, and finally related defect structures will be discussed.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al. : Date: September 25, 1995  
Serial No.: 08/303,561 : Group Art Unit: 1105  
Filed: September 9, 1994 : Examiner: D. McGinty  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

SUBMISSION AFTER FINAL REJECTION UNDER 37 CFR 1.129(a)

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

In response to the final rejection dated March 29, 1995,  
please consider the following:

The above-identified application has been pending for at least  
two years as of June 8, 1995 and has been finally rejected and a  
Notice of Appeal has not been filed. Applicants request that the  
amendment submitted herewith be considered on the merits under 37  
CFR 1.129(a).

Please charge deposit account 09-0468 the fee of \$730.00 under  
37 CFR 1.17(r) and any other fee necessary to enter this paper and  
the amendment submitted herewith.

If applicants are not entitled to entry of the amendment  
YO987-074BY 1

S.N. 08/303,561

submitted herewith, applicants request this paper be considered a Notice of Appeal and request that deposit account 09-0468 be charged any fee necessary to enter this Notice of Appeal.

Respectfully submitted,

A handwritten signature in cursive script, appearing to read "Daniel P. Morris".

By: Daniel P. Morris  
Attorney  
Registration No. 32,053

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, NY  
Tel. (914) 945-3217  
FAX (914) 945-3281

/ma

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
Bednorz et al. : Date: September 26, 1995  
Serial No.: 08/303,561 : Group Art Unit: 1105  
Filed: September 9, 1994 : Examiner: D. McGinty  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Timothy Dinger, being duly sworn, do hereby depose and state:

That I received a B.S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M.S. degree (1983) and a PhD. degree (1986), both in Material Science from the University of California at Berkley.

That I have worked as a research staff member in Material Science at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1986 to the present.

That I have worked in the fabrication of and characterization of high temperature superconductor materials from 1987 to 1991.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Müller,

YO987-074BY

which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Müller behave in a similar way, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by claims 24-26, 86-90 and 96-108, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Müller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

By: Timothy Dinger  
Timothy Dinger

Sworn to before me this 26th day of September, 1995



DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 488676  
Qualified in Westchester County 9/97  
Commission Expires March 16, 1997



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
Bednorz et al. : Date: September 26, 1995  
Serial No.: 08/303,561 : Group Art Unit: 1105  
Filed: September 9, 1994 : Examiner: D. McGinty  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, David B. Mitzi, being duly sworn, do hereby depose and  
state:

That I received a B.S.E. degree in Electrical  
Engineering/Engineering Physics (1985) from Princeton University  
and a PhD. degree, in Applied Physics (1990) from Stanford  
University, California.

That I have worked as a research staff member in Solid State  
Chemistry at the Thomas Watson Research Center of the International  
Business Machines Corporation in Yorktown Heights, NY from 1990 to  
the present.

That I have worked in the fabrication of and characterization of  
high temperature superconductor and related materials from 1990 to  
the present.

That I have reviewed the above-identified patent application and


YO987-074BY

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Müller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

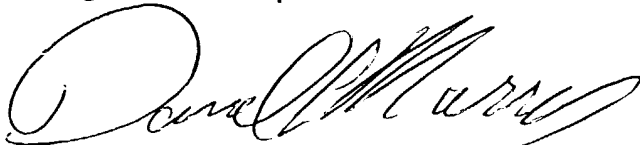
That all the high temperature superconductors which have been developed based on the work of Bednorz and Müller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by claims 24-26, 86-90 and 96-108, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Müller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

By:

  
David B. Mitzi

Sworn to before me this 26th day of September, 1985



DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4888676  
Qualified in Westchester County  
Commission Expires March 16, 1997

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J. Bednorz et al.

Serial No.: 08/303,561

Filed: September 9, 1994

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Group Art Unit: 1105

Examiner: D. McGinty

PETITION AND FEE FOR EXTENSION OF TIME (37 CFR 1.136(a))

Commissioner of Patents and Trademarks  
Washington, DC 20231

Sir:

1. This is a petition for an extension of the time to respond to the Office Letter mailed on March 29, 1995 for a period of 3 months.
2. Applicant is other than a small entity.
3. Extension period and fee:

| <u>(months)</u>                                  | <u>Fee for other than<br/>small entity</u> |
|--|--|
| <input type="checkbox"/> one month               | \$ 110.00                                  |
| <input type="checkbox"/> two months              | \$ 370.00                                  |
| <input checked="" type="checkbox"/> three months | \$ 870.00                                  |
| <input type="checkbox"/> four months             | \$1,360.00                                 |

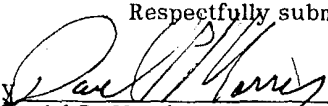
Fee: \$ 870.00

4. An amendment  
☒ is filed herewith.  
☐ has been filed.

5. Fee Payment  
☒ Charge fee to Deposit Account No. 09-0468 and for any additional extension fee required or credit for any excess fee paid. A duplicate copy of this sheet is enclosed.

Date: September 26, 1995

Respectfully submitted,

By   
Daniel P. Morris  
Attorney  
Registration No. 32,053

Telephone: (914) 945-3217  
Fax: (914) 945-3281

From:  
IBM Corporation  
Intellectual Property Law  
P.O. Box 218  
Yorktown Heights, NY 10598

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J. Bednorz et al.

Serial No.: 08/303,561

Group No.: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

ASSOCIATE POWER OF ATTORNEY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Please recognize Daniel P. Morris, No. 32,053 as associate attorney in the prosecution of the above-identified application for Letters Patent, with full power: to prosecute said application; to make alterations and amendments therein; to receive all notices, communications and said Letters Patent at the address indicated below; and to transact all business in the U.S. Patent and Trademark Office connected therewith.

Please forward all correspondence to:

Daniel P. Morris  
IBM CORPORATION  
Intellectual Property Law Dept.  
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Yorktown Heights, NY 10598  
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Please address any telephone calls to Daniel P. Morris at (914) 945-3217, and send any facsimile transmissions to (914) 945-3281.

Date: September 26, 1995

Respectfully submitted,

By Jackson E. Stanland  
Jackson E. Stanland  
Attorney of Record  
Registration No. 24,444

From:

IBM Corporation  
Intellectual Property Law  
P.O. Box 218  
Yorktown Heights, N.Y. 10598

Telephone: (914) 945-3186  
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Bednorz et al.

Serial No.: 08/303,561

Group No.: 1105

Filed: September 9, 1994

Examiner: D. McGinty

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

ASSOCIATE POWER OF ATTORNEY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Please recognize William B. Porter, Reg. No. 33,135 as associate attorney in the prosecution of the above-identified application for Letters Patent, with full power: to prosecute said application; to make alterations and amendments therein; to receive all notices, communications and said Letters Patent at the address indicated below; and to transact all business in the U.S. Patent and Trademark Office connected therewith.

Please forward all correspondence to:

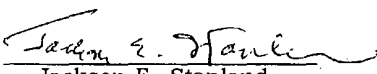
William B. Porter  
IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, NY 10598

Please address any telephone calls to William B. Porter at (914) 945-3255, and send any facsimile transmissions to (914) 945-3281.

Date: September 26, 1995

Respectfully submitted,

By

  
Jackson E. Stanland  
Attorney of Record  
Registration No. 24,444

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IBM Corporation  
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Fax: (914) 945-3281



**UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office**

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| SERIAL NUMBER | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO.   |
|---------------|-------------|----------------------|-----------------------|
| 08/303,561    | 09/09/94    | BEDNORZ              | J Y0987074B <i>BY</i> |

11M1/0329

DANIEL P. MORRIS  
IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPARTMENT  
P O BOX 218  
YORKTOWN HEIGHTS NY 10598

ME GINTY, P  
**EXAMINER**

**ART UNIT** **PAPER NUMBER**

1105

*46*

03/29/95

**DATE MAILED:**

This is a communication from the examiner in charge of your application.  
COMMISSIONER OF PATENTS AND TRADEMARKS

*DOE 6/29/95  
FINAL*

☒ This application has been examined ☐ Responsive to communication filed on \_\_\_\_\_ ☒ This action is made final.

A shortened statutory period for response to this action is set to expire 3 month(s), \_\_\_\_\_ days from the date of this letter.  
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

**Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:**

- |   |   |
|---|---|
| 1. <input type="checkbox"/> Notice of References Cited by Examiner, PTO-892.        | 2. <input type="checkbox"/> Notice of Draftsman's Patent Drawing Review, PTO-948. |
| 3. <input type="checkbox"/> Notice of Art Cited by Applicant, PTO-1449.             | 4. <input type="checkbox"/> Notice of Informal Patent Application, PTO-152.       |
| 5. <input type="checkbox"/> Information on How to Effect Drawing Changes, PTO-1474. | 6. <input type="checkbox"/> _____   |

**Part II SUMMARY OF ACTION**

1. ☒ Claims 24-26, 86-90, & 96-108 are pending in the application.  
Of the above, claims \_\_\_\_\_ are withdrawn from consideration.
2. ☒ Claims 1-23, 27-85, & 91-95 have been cancelled.
3. ☐ Claims \_\_\_\_\_ are allowed.
4. ☒ Claims 24-26, 86-90, & 96-108 are rejected.
5. ☐ Claims \_\_\_\_\_ are objected to.
6. ☐ Claims \_\_\_\_\_ are subject to restriction or election requirement.
7. ☐ This application has been filed with informal drawings under 37 C.F.R. 1.85 which are acceptable for examination purposes.
8. ☐ Formal drawings are required in response to this Office action.
9. ☐ The corrected or substitute drawings have been received on \_\_\_\_\_. Under 37 C.F.R. 1.84 these drawings are ☐ acceptable; ☐ not acceptable (see explanation or Notice of Draftsman's Patent Drawing Review, PTO-948).
10. ☐ The proposed additional or substitute sheet(s) of drawings, filed on \_\_\_\_\_, has (have) been ☐ approved by the examiner; ☐ disapproved by the examiner (see explanation).
11. ☐ The proposed drawing correction, filed \_\_\_\_\_, has been ☐ approved; ☐ disapproved (see explanation).
12. ☒ Acknowledgement is made of the claim for priority under 35 U.S.C. 119. The certified copy has ☐ been received ☐ not been received  
☒ been filed in parent application, serial no. 08 105 3302; filed on 5-22-87.
13. ☐ Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.
14. ☐ Other

**EXAMINER'S ACTION**

**Part III DETAILED ACTION**

1. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

**Priority**

2. Acknowledgment is made of applicant's claim for priority under 35 U.S.C. § 119. The certified copy has been filed in parent application, Serial No. 08/053,307, filed on April 23, 1993 as paper no. 28.

3. However, a review of that certified copy, which is in English, indicates that it does not support the present assertion of priority. Support is not found in that certified copy for the invention as presently claimed. See MPEP 201.13 et seq. and 201.14 et seq.

**Claim Rejections - 35 USC § 112**

4. The specification is objected to under 35 U.S.C. § 112, *first paragraph*, as the specification, as originally filed, does not support the invention as is now claimed.

a. The language of claim 103 is not supported by the original specification.

b. Claims 103-108 are rejected under 35 U.S.C. § 112, *first paragraph*, for the reasons set forth in the objection to the specification.

5. The specification is objected to under 35 U.S.C. § 112, *first paragraph*, as failing to provide an enabling disclosure commensurate with the scope of the claims.

a. The present specification is only enabled for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_y$ . The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases. See In re Fisher, 166 USPQ 18, 24; and In re Angstadt and Griffen, 190 USPQ 214, 218.

See also, In re Colianni, 195 USPQ 150, 153, 154 (CCPA 1977) (J. Rich). Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 USC 112. See In re Cook, 169 USPQ 298, 302; and Cosden Oil v. American Hoechst, 214 USPQ 244, 262,. Merely reciting a desired result does not overcome this failure. See In re Corkill, 226 USPQ 105, 1009. In particular, the question arises: Will any layered perovskite material containing copper exhibit superconductivity? Also, does any stoichiometric combination of rare earth, an alkaline earth, and copper elements result in an oxide superconductor?

b. It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood. Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion", Brenner v. Manson, 383 US 519, 148 USPQ 689.

c. Claims 24-26, 86-90, and 96-108 are rejected under 35 U.S.C. § 112, *first paragraph*, for the reasons set forth in the objection to the specification.

6. Claims 86-87 and 96-108 are rejected under 35 U.S.C. § 112, *second paragraph*, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

a. The terms "layer-type", "perovskite-like", "rare-earth-like" are vague and confusing. The question arises: What is meant by these terms?



b. Claims 101 and 107 recite "at least one element in a nonstoichiometric atomic proportion". The question arises: How can any element be of nonstoichiometric atomic proportion?

c. The language of claim 103 is confusing. The question arises: What is meant by the term "the composition having a superconductive/resistive transition defining a superconductive/resistive-transition temperature range"?

*Claim Rejections - 35 USC § 102*

7. Claims 24-26, 86-90, and 96-108 are rejected under 35 U.S.C. § 102(a) as being anticipated by Asahi Shinbum, International Satellite Edition (London), November 11, 1986 (hereinafter, "the Asahi Shinbum article").

a. As discussed in paper no. 20 of the ancestral application, 07/053,307, it is not fully clear to what exact date applicants are entitled. Based on the record, nonetheless, that date would appear to be no later than around December 13, 1986, the date samples were tested in the US to show superconductivity. See MPEP 715 et seq. The Asahi Shinbum article was published on November 28, 1986.

b. The reference confirms superconductivity in an oxide compound of La and Cu with Ba having a structure of the so-called perovskite structure. Although the reference fails to teach use of the testing of zero resistance for confirming superconductivity, it inherently must have been used because it is one of two methods used for testing for superconductivity (the other being diamagnetism). Accordingly, the burden of proof is upon the applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference. See In re Brown, 173 USPQ 685, 688; In re Best, 195 USPQ 430; and In re Marosi, 218 USPQ 289, 293.

Serial Number: 08/303,561

-5-

Art Unit: 1105

*Claim Rejections - 35 USC § 103*

8. Claims 24-26, 86-90, and 96-108 are rejected under 35 U.S.C. § 103 as being unpatentable over the Asahi Shinbum article.

a. The reference is relied upon as set forth in the previous rejection. This reference may differ from the present claims in that it may fail to disclose the presently claimed method of "causing an electric current to flow in the superconductor element". It was notoriously well-known in the art of superconductors that a method of utilizing superconductive materials was to cause an electric current to flow in the material while it is cooled below its transition temperature. See MPEP 706.02(a). Accordingly, it would have been well within the purview of one of ordinary skill to use the present claimed method with the materials disclosed by the reference. One would have been motivated to cool the material of the reference to below the transition temperature and cause electric current to flow in the material to provide electricity without resistance. Accordingly, the present claims are unpatentable in view of the prior art of record.

*Possibly Allowable Subject Matter*

9. It is noted that the applicants were awarded the Nobel Prize for their work in this area. The record is not deemed to indicate, however, that the Asahi Shinbum article was predicated by the applicants' earlier conception and/or reduction to practice in this country. The presently claimed invention also is non-enabling and indefinite for the reasons set forth above.

Serial Number: 08/303,561  
Art Unit: 1105

-6-

10. To possibly overcome the above rejections, the following amendments are suggested:

a. 109 (New). A method comprising the steps of:  
forming a composition of the formula  $Ba_xLa_{5-x}Cu_5O_y$ , wherein  $x$  is from about 0.75 to about 1 and  $y$  is the oxygen deficiency resulting from annealing said composition at temperatures from about 540°C to about 950°C and for times of about 15 minutes to about 12 hours, said composition having a metal oxide phase which exhibits a superconducting state at a critical temperature in excess of 26°K;

maintaining the temperature of said composition at a temperature less than said critical temperature to induce said superconducting state in said metal oxide phase; and

passing an electrical supercurrent through said composition while said metal oxide phase is in said superconducting state.

b. Cancel claims 24-26, 86-90, and 96-108.

11. The following is an Examiner's statement of reasons for the indication of possibly allowable subject matter:

a. The Asahi Shinbun article teaches in general that perovskite-like compounds of La, Cu, and Ba have a  $T_c$  of 30°K, but that article apparently does not teach the particular formula in the amendment suggested above. The examples in the present specification are deemed to show criticality for that formula in that suggested amendment.

b. Support for the proposed amendment is found at p. 20, line 1, through p. 25, line 5, and in Figure 3.

12. This indication of possibly allowable subject matter is subject to further consideration and review.

#### **Conclusion**

h13. This is a file wrapper continuation of applicant's earlier application S.N. 08/060,470. All claims are drawn to the same invention claimed in the earlier application and could have been finally rejected on the grounds or art of record in the next Office action if they had been entered in the earlier application. Accordingly, **THIS ACTION IS MADE FINAL** even though

Serial Number: 08/303,561

-7-

Art Unit: 1105

it is a first action in this case. See M.P.E.P. § 706.07(b). Applicant is reminded of the extension of time policy as set forth in 37 C.F.R. § 1.136(a).

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS FINAL ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS ACTION. IN THE EVENT A FIRST RESPONSE IS FILED WITHIN TWO MONTHS OF THE MAILING DATE OF THIS FINAL ACTION AND THE ADVISORY ACTION IS NOT MAILED UNTIL AFTER THE END OF THE THREE-MONTH SHORTENED STATUTORY PERIOD, THEN THE SHORTENED STATUTORY PERIOD WILL EXPIRE ON THE DATE THE ADVISORY ACTION IS MAILED, AND ANY EXTENSION FEE PURSUANT TO 37 C.F.R. § 1.136(a) WILL BE CALCULATED FROM THE MAILING DATE OF THE ADVISORY ACTION. IN NO EVENT WILL THE STATUTORY PERIOD FOR RESPONSE EXPIRE LATER THAN SIX MONTHS FROM THE DATE OF THIS FINAL ACTION.

14. Any amendment in response to this Office Action must NOT include any new matter. See MPEP 608.04 and 706.03(o).

15. All of the references cited in this application indicate the level of skill in the relevant art at the time the invention was made.

16. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Douglas J. McGinty, whose telephone number is (703) 308-3805. The examiner normally can be reached on Monday through Friday from 8:30 A.M. to 5:00 P.M., Eastern time. If reasonable attempts to reach the examiner by telephone are unsuccessful, however, the examiner's supervisor, Mr. Paul Lieberman, can be reached at (703) 308-2523. Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

17. The fax number for this Group is (703) 305-3599.

*DM*  
Douglas J. McGinty  
March 28, 1995  
303561.1

PAUL LIEBERMAN  
SUPERVISORY PRIMARY EXAMINER  
ART UNIT 115

Filing: Claim to Priority Under 35 USC 119 w/European Patent  
 Appn and Suppl. Declaration & Power of Attorney, Info. Discl. time (4 mos.)  
 State, PTO 1440 Form, 41 references, Ext. of time (4 mos.)  
**PLEASE STAMP & RETURN TO US**

In re application of: J. Georg Bednorz and K. Alex Mueller

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH...

Serial No 07/053,307; Docket No.: YO987-074 Atty.: JDE

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_ No. of pages of claims: \_\_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification: \_\_\_\_\_

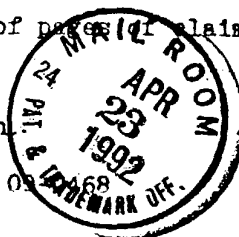
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C. Alex Mueller

VING HIGH...

JDE

of claims \_\_\_\_\_



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EXPRESS MAIL NEXT DAY SERVICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J. Georg Bednorz and K. Alex Mueller

Serial No: 07/053,307

Group No.: 115

Filed: 22 May 1987

Examiner: John Boyd

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION  
Commissioner of Patents and Trademarks

Washington, D.C. 20231

EXPRESS MAIL CERTIFICATE

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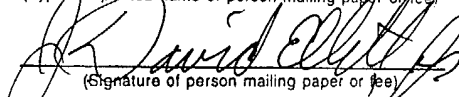
I hereby certify that the following *attached* paper or fee

- (1) Claim to Priority Under 35 U.S.C. Section 119 with certified copy of European Patent Application Serial No. 8710.0961.9 and supplemental Declaration and Power of Attorney attached;
- (2) Information Disclosure Statement with Appendices A and B and Form PTO 1449 attached;
- (3) Copies of 41 references listed in Form PTO 1449
- (4) Petition and Fee for Extension of Time; and
- (5) Return Post Card

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

J. David Ellett, Jr. (Reg. No. 27,875)

(Typed or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

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NOTE: The label number need not be placed on each page. It should, however, be placed on the first page of each separate document, such as, a new application, amendment, assignment, and transmittal letter for a fee, along with the certificate of mailing by "Express Mail." Although the label number may be on checks, such a practice is not required. In order not to deface formal drawings it is suggested that the label number be placed on the back of each formal drawing or the drawings be accompanied by a set of informal drawings on which the label number is placed.

DOCKET NO. YO987-074

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

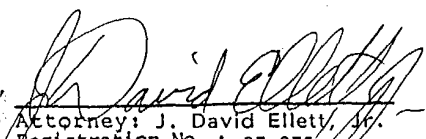
In re application of : Date: April 23, 1992  
 J. Georg Bednorz and :  
 K. Alex Mueller : Group Art Unit: 115  
 : Examiner: John Boyd  
 Serial No.: 07/053,307 :  
 : IBM Corporation  
 Filed: 22 May 1987 : Intellectual Property Law Department  
 : P.O. Box 218  
 For: NEW SUPERCONDUCTIVE : Yorktown Heights, N.Y. 10598  
 COMPOUNDS HAVING HIGH  
 TRANSITION TEMPERATURE, AND  
 METHODS FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
 Washington, D.C. 20231

PETITION AND FEE FOR EXTENSION OF TIME (37 CFR 1.136(a))

1. This is a petition for an extension of the time to file an Appellant's Brief in an appeal dated 28 October 1991 of a Decision by the Primary Examiner finally rejecting claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive of the application identified above for a period of four (4) months from 28 December 1991 to and including 28 April 1992.
2. Applicant is other than a small entity.
3. Extension: Four months;  
 Fee (for other than a small entity). \$ 1,280.00
4. An Information Disclosure Statement and a Claim for Priority Under 35 U.S.C. Section 119 are filed herewith. A Request for Filing a File-Wrapper-Continuing Divisional Application Under 37 CFR 1.62 and a Preliminary Amendment are to be filed on or before 28 April 1992. The subject application on appeal is to be abandoned in favor of the divisional application upon the granting of a filing date to the divisional application.
5. Fee payment  
☒ Charge fee to Deposit Account No. 09-0468 and for any additional extension fee required or credit for any excess fee paid. A duplicate of this petition is attached.

Respectfully submitted,

By:   
 Attorney: J. David Ellett, Jr.  
 Registration No.: 27,875

Docket No.: Y0987-074

Telephone No.: (914) 241-4060

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|                                    |   |                     |
|------------------------------------|---|---------------------|
| In re Patent Application of        | : |                     |
| J. GEORG BEDNORZ and               | : | Art Unit: 115       |
| K. ALEX MUELLER                    | : |                     |
| Serial No.: 07/053,307             | : | Examiner: John Boyd |
| Filed: 22 May 1987                 | : |                     |
| For: NEW SUPERCONDUCTIVE COMPOUNDS | : |                     |
| HAVING HIGH TRANSITION             | : |                     |
| TEMPERATURE, AND METHODS FOR       | : |                     |
| THEIR USE AND PREPARATION          | : |                     |

CLAIM TO PRIORITY UNDER 35 U.S.C. Section 119

Honorable Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

Sir:

By their attorneys, the applicants in the application identified above hereby claim under 35 U.S.C. Section 119 the priority of an application filed on 23 January 1987 in their behalf in the European Patent Office as European patent application Serial No. 87100961.9 ("the European '961 patent application"). Submitted herewith are: (1) a certified copy of the European '961 application upon which the claim to priority is based; and (2) a supplemental Declaration and Power of Attorney for the application duly executed by the applicants, Drs. Bednorz and Mueller on 4 February 1992 and 28 February 1992, respectively, in which a claim of priority under 35 U.S.C. Section 119 to the European '961 application is made.

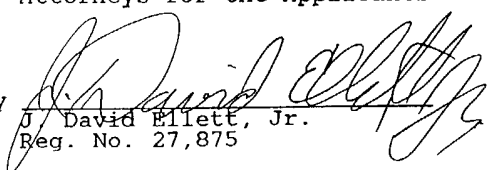


As noted in an Information Disclosure Statement filed herewith, three persons were identified as joint inventors in the European '961 application: J. Georg Bednorz and K. Alex Mueller - the applicants in the subject United States application - and Masaaki Takashige, a Japanese citizen residing in Ruschlikon, Switzerland at the time of filing the '961 application. The difference in inventorship arose under the circumstances of the present case because patent laws of the United States and the European patent convention differ, as discussed in the Information Disclosure Statement.

Respectfully submitted,

Attorneys for the Applicants

by

  
J. David Ellett, Jr.  
Reg. No. 27,875

IBM Thomas J. Watson Research Center  
Intellectual Property Law Department  
P.O. Box 218  
Yorktown Heights, N.Y. 10598

Tel. (914) 241-4060

23 April 1992

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### Bescheinigung

### Certificate

### Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Den Haag, den  
The Hague,  
La Haye, le

20 Mars 1987

Der Präsident des Europäischen Patentamts  
Im Auftrag  
For the President of the European Patent Office  
Le Président de l'Office européen des brevets  
p. o.

Y. VAN DER WOUDE-ZOLLER  
Patentanmeldung Nr.  
Patent application no. 87100961.9  
Demande de brevet n°

## DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

DOCKET NO.  
Y0987-074

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name:

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled  
**NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION**

the specification of which (check one)

☐ is attached hereto.☒ was filed on 22 May 1987 asApplication Serial No. 07/053,307

and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed

87100961.9European23 January 1987

(Number)

(Country)

(Day/Month/Year Filed)

☒ Yes ☐ No

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes ☐ No

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes ☐ No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

John A. Jordan (Reg. No. 24,655), Jeffrey L. Brandt (Reg. No. 31,490),

Joseph A. Biela (Reg. No. 30,157), John D. Crane (Reg. No. 25,231)

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Full name of sole or first inventor

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4th February 1992

Inventor's signature

Johannes Georg Bednorz

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28 February 1992

Second inventor's signature

Carl Alexander Mueller

Date

28. 2. 92

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Post Office Address

Same as above

(Supply similar information and signature for third and subsequent joint inventors.)

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|                                    |   |                     |
|------------------------------------|---|---------------------|
| In re Patent Application of        | : |                     |
| J. GEORG BEDNORZ and               | : | Art Unit: 115       |
| K. ALEX MUELLER                    | : |                     |
| Serial No.: 07/053,307             | : | Examiner: John Boyd |
| Filed: 22 May 1987                 | : |                     |
| For: NEW SUPERCONDUCTIVE COMPOUNDS | : |                     |
| HAVING HIGH TRANSITION             | : |                     |
| TEMPERATURE, AND METHODS FOR       | : |                     |
| THEIR USE AND PREPARATION          | : |                     |

INFORMATION DISCLOSURE STATEMENT UNDER 37 CFR 1.97

Honorable Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

Sir:

Pursuant to 37 CFR 1.97, the attorneys for the applicants submit the following statement.

The attorneys for the applicants hereby bring to the attention of the United States Patent and Trademark Office the following publications and unpublished manuscripts which are broadly related to the field of the instant invention:

Publications and Unpublished Manuscripts

J. B. Goodenough and J. M. Longo, *Magnetic and Other Properties of Oxides and Related Compounds*, in Landolt-Bornstein New Series, vol III/4a, K.-H. Hellwege and A. M. Hellwege, eds. (Springer-Verlag 1970), pages 261-314;

P. W. Anderson, *Comments on Solid State Physics*, vol. II, pages 193-197, (February/March 1970);

R. Englman, *The Jahn-Teller Effect in Molecules and Crystals*, (Wiley-Interscience, 1972), pages 139-141, 164-181, 249-265;

B. K. Chakraverty, *Journal de Physique-Lettres*, vol. 40, pages L-99 - L-100, (March 1979);

G. Deutscher et al., *Physical Review B*, vol. 21, pages 5041-5047, (1 June 1980);

K. A. Muller et al., *Physical Review Letters*, vol. 45, pages 832-835, (8 September 1980);

R. A. Buhrman et al., in *AIP Conference Proceedings, Inhomogeneous Superconductors - 1979*, (Berkeley Springs, W. V.), D. U. Gubser et al., pages 207-215 (1980);

T. D. Thanh et al., *Applied Physics*, vol. 22, pages 205-212 (1980);

C. Methfessel and S. Methfessel, in *Proceedings of the IV Conference on Superconductivity in d- and f- Band Metals*, W. Buckel and W. Weber, eds. Kernforschungszentrum, Karlsruhe, 1982), pages 393-399;

A. Baratoff et al., in *Proceedings of the IV Conference on Superconductivity in d- and f- Band Metals*, W. Buckel and W. Weber, eds. Kernforschungszentrum, Karlsruhe, 1982), page 419;

J. Muller, *Rep. Prog. Phys.*, vol. 43, pages 642-687, (1980);

M. Suzuki et al., *Shinku*, vol. 24 pages 67-75, (1981), [in Japanese];

K. A. Muller et al., *Physical Review Letters*, vol. 47, pages 138-142, (13 July 1981);

Y. Enomoto et al., *Japanese Journal of Applied Physics*, vol. 20, pages L661-L664, (September 1981);

B. K. Chakraverty, *Journal de Physique* vol. 42, pages 1351-1356, (September 1981);

L. Er-Rakho et al., *Journal of Solid State Chemistry*, vol. 37, pages 151-156, (1981);

A. Baratoff and G. Binnig, *Physica*, vol. 108B, pages 1335-1336, (1981);

L. F. Mattheiss and D. R. Hamann, *Physical Review B*, vol. 26, pages 2686-2689, (1 September 1982);

L. F. Mattheiss and D. R. Hamann, *Physical Review B*, vol. 28, pages 4227-4241, (15 October 1983);

K.-H. Hock et al., *Helvetica Physica Acta*, vol. 56, pages 237-243, (1983);

N. Nguyen et al., *Journal of the Physics and Chemistry of Solids* vol. 44, pages 389-400, (1983);

D. R. Bowman and D. Stroud, *Physical Review Letters*, vol 52, pages 299-302, (23 January 1984);

M. Tinkham et al., *Workshop on Problems in Superconductivity*, Copper Mountain, CO, pages 12-22, (1984);

B. Batlogg, *Physica*, vol. 126B, pages 275-279, (1984);

C. Ebner and D. Stroud, *Physical Review B*, vol. 31, pages 165-171, (1 January 1985);

M. R. Harrison et al., *Philosophical Magazine B*, vol. 52, pages 679-699, (1985);

E. Stocker and J. Buttet, *Solid State Communications*, vol. 53, pages 915-917, (1985);

C. Van Haesendonck and Y. Bruynseraede, *Physical Review B*, vol. 33, pages 1684-1690, (1 February 1986);

H. R. Ott, *Unconventional Superconductivity*, Zurich Physical Society Seminar, Zurich, (13 February 1986), [in German];

T. Ogushi and Y. Osono, *Applied Physics Letters*, vol. 48, pages 1167-1168, (28 April 1986);

S.-I. Uchida et al., "High  $T_c$  Superconductivity of La-Ba-Cu Oxides" unpublished nine-page manuscript bearing date of 22 November 1986;

*Asahi Shinbun*, International Satellite Edition (London), 28 November 1986, (in Japanese with English translation);

H. Takagi et al., "High- $T_c$  Superconductivity of La-Ba-Cu Oxides. II-Specification of the Superconducting Phase", unpublished nine-page manuscript bearing date of 8 December 1986;

S.-I. Uchida et al., "High- $T_c$  Superconductivity of La-Ba-Cu Oxides. III-Electrical Resistivity Measurement" unpublished nine-page manuscript (page 7 missing) bearing date of 22 December 1986;

K. Kishio et al., "New High temperature Superconducting Oxides.  $(La_{1-x}Sr_x)_2CuO_{4-\delta}$  and  $(La_{1-x}Ca_x)_2CuO_{4-\delta}$ " unpublished four-page manuscript bearing date of 22 December 1986;

C. W. Chu et al., "Superconductivity Above 52K in the La-Ba-Cu-O System," unpublished fourteen-page manuscript bearing date of 30 December 1986;

W. Sullivan, *New York Times*, 31 December 1986, page A1, cols. 2-3 and A13, cols. 1-2;

S.-I. Uchida et al., "High- $T_c$  Superconductivity of La-Ba(Sr)-Cu Oxides. IV - Critical Magnetic Fields," unpublished ten-page manuscript bearing date of 8 January 1987;

S. Kanbe et al., "Superconductivity and Lattice Parameters in  $(La_{1-x}Sr_x)_2CuO_{4-\delta}$  Solid Solution System" unpublished four-page manuscript bearing date of 13 January 1987;

H. Takagi et al., "Influence of the Oxygen Deficiency on the Electrical Resistivity in High- $T_c$  Superconducting Oxides  $(LaBa)_2CuO_{4-y}$ " unpublished eight-page manuscript bearing date of January 1987; and

Z. Zhao et al., "High  $T_c$  Superconductivity of Sr(Ba)La-Cu Oxides," unpublished eleven-page manuscript bearing date of 21 January 1987.

The publications and unpublished manuscripts identified above are listed on form PTO 1449 which accompanies this statement. Copies of the publications and unpublished manuscripts are being submitted with this statement.

The attorneys for the applicants take no position on whether or not any particular document cited in the present Disclosure Statement and listed on form PTO 1449 constitutes prior art relative to the subject invention with respect to some particular provision of Title 35 of the United States Code. As discussed in detail below, for example, it is the position of the attorneys that a number of the documents identified above bearing dates of less than a year before the filing date of the subject application to the extent they include material which might otherwise appear to be relevant to the invention of the application are essentially only describing the work of the applicants in the

subject application and so do not constitute prior art against the application under United States law.

The two publications discussed briefly in the following two paragraphs concerned certain families of lanthanum copper oxide compounds.

The publication by Er-Rakho et al. in Journal of Solid State Chemistry, volume 37, pages 151-156 (1981), concerned a series of defect perovskites having the general formula  $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$ , where Ln = Y, Pr, Nd, Sm, Eu, Gd, Er, and Yb. In the case of  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$ , the value of y reportedly varied with oxygen pressure to which the compound was exposed during an anneal at 400°C.

According to an English-language abstract, the publication by N. Nguyen et al. in the Journal of the Physics and Chemistry of Solids, volume 44, pages 389-400 (1983), concerned the magnetic and electron transport properties of certain mixed valence copper oxides having the general formula  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-x/2+\delta}$ , where  $0 \leq x \leq 1.20$ . The publication is in French and the attorneys for the applicants do not have an English translation. Table 1 on page 390 appears to give the unit cell dimensions for the compound with various specific values for x and  $2\delta$ . According to the abstract, a progressive evolution of the conductivity from a semiconductor to a semimetallic behavior was observed as the amount of copper in the trivalent state increased.

In response to a request in section 24 of the Office Action of 8 August 1990 for the subject application regarding so-called "preprints," the nine unpublished manuscripts identified below have been located which bear on their face



dates in advance of the priority date to which the subject application is entitled:

AUTHORS

DATE FROM FACE OF MANUSCRIPT

|                        |                  |
|------------------------|------------------|
| 1) S.-I. Uchida et al. | 22 November 1986 |
| 2) H. Takagi et al.    | 8 December 1986  |
| 3) S.-I. Uchida et al. | 22 December 1986 |
| 4) K. Kishio et al.    | 22 December 1986 |
| 5) C. W. Chu et al.    | 30 December 1986 |
| 6) S.-I. Uchida et al. | 8 January 1987   |
| 7) S. Kanbe et al.     | 13 January 1987  |
| 8) H. Takagi et al.    | 17 January 1987  |
| 9) Z. Zhao et al.      | 21 January 1987. |

An electronic-mail note dated 17 December 1986 from Dr. Richard Greene of IBM to the applicants suggests that the unpublished manuscripts bearing the dates 22 November and 8 December were in the hands of Dr. Greene on 16 December 1986. A copy of a printout of the note of 17 December 1986 is attached as Appendix A.

An electronic-mail note dated 7 January 1987 from Dr. Paul Grant of IBM to the applicants and Dr. Greene described a meeting of an Applied Physics Journal Club at Stanford University held on the day of the note. A copy of a printout of the 7 January 1987 note is attached as Appendix B. Reference was made to a "Bell preprint" and to two preprints of Chu. Reference was also made to an article in the New York Times and to an article in the Biejing People's Daily of mid-December.

A copy of an unpublished manuscript by Chu et al. bearing the date 30 December 1986 is submitted with this statement. The attorneys for the applicants do not have copies of any unpublished manuscript which might correspond to a second "preprint" of Chu or to the "Bell preprint" referred to in the note of 7 January 1987. A copy of an article in the New York Times edition of 31 December 1986 concerning superconductivity is submitted with this statement. The attorneys for the applicants do not have a copy of the article in the Beijing People's Daily referred to in the note of 7 January 1987.

Each of the nine unpublished manuscripts identified above expressly attributes the discovery of superconductivity in copper oxide materials to the present applicants. For example, the unpublished manuscript by Uchida et al. bearing the date 22 November 1986 stated on page 1, line 21 through page 2, line 3 as follows:

Another candidate [superconducting material] is La-Ba-Cu oxide. This material has been investigated extensively by Michel and his coworkers. Quite recently Bednorz and Muller have reported that the Ba-La-Cu-O system with the composition  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_2\text{O}_{5(3-x)}$  is a potential material as the third high-Tc oxide. The resistivity measurement on the polycrystalline samples showed that the sample prepared in a certain condition is superconducting below 13K. The most interesting fact is that the resistivity starts to decrease at 30K with lowering temperature. They suggested that this might correspond to an onset of superconductivity in a part of the sample. [References omitted]

The reference to Bednorz and Muller in the quotation above was accompanied by a citation to the article by the applicants in Zeitschrift fur Physik B-Condensed Matter, Vol. 64, pages 189-193 (September 1986) ("the Bednorz and Muller publication") which is of record in the subject application.

See also the unpublished manuscripts by Takagi et al. bearing the date 8 December 1986 at page 2, lines 1-4 and reference 2; Uchida et al. bearing the date 22 December 1986 at page 2, lines 5-10; Kishio et al. bearing [on the last page] the date 22 December 1986 at page 1, lines 18-21 and references 2 and 3; Chu et al. bearing the date 30 December 1986 at page 3, lines 13-25 and reference 1; Uchida et al. bearing the date 8 January 1987 at page 2, lines 1-3 and reference 1 [evidently a preprint of an article by the applicants and a coworker which appeared in Europhysics Letters, volume 3, pages 379-389 (1987) which in turn refers to the Zeitschrift fur Physik article of the applicants]; Kanbe et al. bearing the date 13 January 1987 at page 1, lines 13-14 and references 1 and 2; Takagi et al. bearing the date 17 January 1987 at page 2, lines 1-6 and reference 1; and Zhao et al. bearing the date 21 January 1987 at page 1, lines 12-14 and reference 1.

Thus, such disclosed in each of the manuscripts identified above as might otherwise appear to be relevant to the invention of the subject application is in fact the work of the applicants Drs. Bednorz and Mueller or derived from the prior work of the applicants, as acknowledged in the manuscripts themselves. As a result, none of the unpublished manuscripts constitutes prior art against the subject application irrespective of whether or not any of the manuscripts might constitute a publication under United States patent law and irrespective of the date the invention was reduced to practice in the United States by or on behalf

of the applicants. The Court of Appeals for the Federal Circuit has held that

Rule 131 ... is only one way of overcoming a reference that is not a statutory bar. An applicant may also overcome a reference by showing that the relevant disclosure is a description of the applicant's own work. [Citations omitted.]

In re Costello and McClean, 219 USPQ 389,391 (Fed. Cir. 1983).

The article in the 28 November 1986 edition of Asahi Shinbun noted that the "possibility of high Tc-superconductivity has been reported by scientists in Switzerland in this spring" and went on to report that Professor Shoji Tanaka had "confirmed" that an oxide of La and Cu with Ba exhibited the Meissner effect, an indication of superconductivity, up to 30K. The article in the 31 December 1986 edition of the New York Times after referring to developments reported by researchers at the University of Houston and A.T. & T. Bell Laboratories, noted that

These developments follow a discovery reported last April by researchers at the I.B.M. Zurich Research Laboratory in Switzerland. Using a combination of copper, oxygen, barium and lanthanum, they achieved superconductivity at 30 degrees Kelvin, opening a new line of attack on the problem.

Later in the article, the I.B.M. findings were attributed to an article by J. G. Bednorz and K. A. Mueller in Zeitschrift fur Physik, Series B. (Contrary to the implication in the New York Times and Asahi Shudron articles, the first publication by Drs. Bednorz and Mueller concerning high Tc superconductivity did not appear in April 1986 or otherwise in the spring of 1986, but appeared in September 1986 with the publication of their Zeitschrift fur Physik B article cited above.) Neither the Asahi Shinbun nor the New York Times article constitutes prior art against the present application since - as evident from the articles themselves

- such as otherwise might appear to be relevant to the subject application was derived from the prior invention of the applicants. Under the doctrine of the Costello and McLean case cited in the preceding paragraph, the articles do not constitute references against the subject application.

The remaining publications identified above were cited either in the Bednorz and Mueller publication or in a publication by Bednorz, Mueller and M. Takashige, in Europhysics Letters, volume 3, pages 379-385 (1987), both of which publications are of record in the subject application. The publications are included in the present Information Disclosure Statement for completeness.

Submitted with this Information Disclosure Statement is a Claim to Priority Under 35 U.S.C. Section 119 for the application. The priority claim is based on European application Serial No. 87100961.9, filed 23 January 1987 ("the European '961 application"). The European '961 application identified as joint inventors Dr. Bednorz and Dr. Mueller - the applicants in the subject United States application - and Masaaki Takashige, a Japanese citizen residing in Ruschlikon, Switzerland at the time of filing the European application. The difference in inventorship between the subject United States application and the European '961 application arose under the circumstances of the present case because patent laws of the United States and the European patent convention differ, as discussed in the following paragraph.

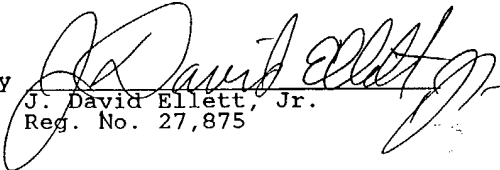
The European patent convention has generally an "absolute novelty" standard of patentability with regard to divulgation of an invention in a publication by the

inventors, whereas United States patent law provides a one-year grace period for filing a patent application following the first description of an invention by the inventors in a publication. In the present case, basic aspects of the invention were described in an article by Drs. Bednorz and Mueller in Zeitschrift fur Physik B-Condensed Matter, Volume 64, pages 189-193 which, as noted above, was published in September 1986. Since the Bednorz and Mueller publication appeared before the '961 European application was filed, aspects of the invention described in the publication were ineligible for patent protection in the European application under the European "absolute novelty" patentability standard. The '961 European application therefore included other material in addition to that described in the Bednorz and Mueller article in support of patentability under the European patent law. In accordance with standard European patent practice, Drs. Bednorz, Mueller and Takashige were designated joint inventors of the subject matter for which patent protection was sought under the European patent convention in the '961 European patent application. In the case of the subject United States application, basic aspects of the invention described in the Bednorz and Mueller publication were not ineligible for patent protection by virtue of the one-year grace period provided by United States patent law. The subject United States application is intended to secure patent protection for fundamental aspects of the invention for which Drs. Bednorz and Mueller are jointly the inventors under principles of United States patent law. A United States patent application may secure the benefit of priority under the International Convention of a foreign patent application having a different inventive entity if the foreign application was regularly filed and the designation of

inventorship in the United States application is correct.  
Payne v. Natta, Pino and Mazzanti, 172 U.S.P.Q. 687, 693  
(Pat. Off. Bd. of Pat. Inter. 1971).

Respectfully submitted,  
Attorneys for the Applicants

by

  
J. David Ellett, Jr.  
Reg. No. 27,875

IBM Thomas J. Watson Research Center  
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P.O. Box 218  
Yorktown Heights, N.Y. 10598

Tel. (914) 241-4060

23 April 1992

FILE: ALL

NOTEBOOK AO

VM/SP CONVERSATIONAL MONITOR SYSTEM

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Date: 17 December 1986, 08:44:19 EST  
From: RGREENE at YKTVMZ  
To: BED at ZURLVM1, KAM at ZURLVM1

Hi Alex and George;

Yesterday I sent you the two Japanese preprints. They find a 30% Meissner effect at 5K and a sharp resistive transition at 29K in their best material. They have identified the same phase as you find but they make their samples by reacting  $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  in various ratios at 1100 degrees C in air for 24 hours. Annealing in a reduced atmosphere destroys the SC. Call me if you want more info but there is not much more in these papers....submission dates 8 DEC and 22 Nov.

Best regards,  
Rick

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FILE: ALL

NOTEBOOK A0

VM/SP CONVERSATIONAL MONITOR SYSTEM

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Date: 7 January 1987, 21:10:27 PST

From: Paul Grant

GRANT at ALMVMC

To: KAM at ZURLVM1

BED at ZURLVM1

Rick Greene

RGREENE at YKTVMZ

Here's a synopsis of the Stanford Journal Club talk today. Rick, Ted said you had received the Bell preprint...could you send me a copy by Federal Express?

\*\*\*\*\*

Today I attended the Applied Physics Journal Club session at Stanford, where Ted Geballe reviewed the situation on BaLaCuO superconductivity. I attend these sessions fairly often, and this was the largest audience I have seen for some time...perhaps in excess of 100 people. Throughout the first part of Ted's presentation, a lot of skepticism was evinced by the audience...Loughlan of quantum hall effect fame was particularly vocal. At the end, although, I think most people were rather bowled over by what they heard. Mac Beasley admitted he wished he was the one who had discovered it. The main points brought out follow (Geballe is well-known for his rambling and disconnected presentation style...but I think I got most things straight):

--The Japanese (and perhaps AT&T Bell) have made the strontium compound with a sharp transition that starts at 40K and is 2K wide with an almost bulk Meissner effect...I am not sure whether this was in resistance, susceptibility or both. The information came to Mac Beasley by phone either today or yesterday.

--A low temperature critical field of 80 tesla (yes, eighty) was measured at the Japanese equivalent of the Bitter National Magnet Lab (didn't get the exact name of the institute).

--The Chu work from both preprints was reviewed. To me, the data did not seem the best quality. Chu defined the onset temperature as that when the sample resistance fell 1% below its "plateau value." Beasley remarked with this convention, the Takagi resistance data implied a threshold value of 45K.

Miscellaneous comments:

I asked Geballe what he thought of the NY Times article. I got the strong impression he felt the Zurich work should have been stressed more and in fact I think he passed this feeling on to the Murray Hill people.

APPENDIX B

FILE: ALL

NOTEBOOK A0

VM/SP CONVERSATIONAL MONITOR SYSTEM

I asked whether he or Mac had done any film work yet. They have a student (Sun) working on preparation for the last 3-4 weeks. I don't think they've had success yet...to press further would have been indelicate. They are trying both sputtering and e-beam evaporation.

What was news to me is that Goodenough at Lincoln Lab worked on the 1:1 BaLaCuO in the 50's or 60's. Even its resistance was measured, but only down to 100K.

Finally, Geballe showed a foil proving the NY Times had been scooped! The Beijing People's Daily ran in mid-December an article that claimed the local university/institute had obtained a BaLaCuO compound with a  $T_c = 70K$ ! The foil was in Chinese characters but one of the students in the audience provided a spontaneous translation.

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|   |         |  |            |
|---|---------|--|------------|
| LIST OF REFERENCES CITED BY APPLICANT<br>(Use several sheets if necessary)  |         | ATTY. DOCKET NO.   | SERIAL NO. |
|   |         | YO987-074  | 07/053,307 |
|   |         | APPLICANT  |            |
|   |         | J. Georg Bednorz and K. Alex Mueller   |            |
|   |         | FILING DATE  | GROUP      |
|   |         | 22 May 1987  | 115        |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |         |  |            |
|   | AA<br>1 | J. B. Goodenough and J. M. Longo, <u>Magnetic and Other Properties of Oxides and Related Compounds</u> , in Landolt-Bornstein New Series, vol. III/4a,   |            |
|   |         | K.-H. Hellwege and A. M. Hellwege, eds. (Springer-Verlag 1970),  |            |
|   |         | pages 261-314.   |            |
|   | AC<br>1 | P. W. Anderson, <u>Comments on Solid State Physics</u> , vol. II, pp. 193-197  |            |
|   |         | (February/March 1970).   |            |
|   | AD<br>1 | R. Englman, <u>The Jahn-Teller Effect in Molecules and Crystals</u> ,  |            |
|   |         | (Wiley-Interscience, 1972), pp. 139-141, 164-181, 249-265.   |            |
|   | AE<br>1 | B. K. Chakraverty, <u>Journal de Physique-Lettres</u> , vol. 40, pp. L-99 - L-100,   |            |
|   |         | (March 1979).  |            |
|   | AF<br>1 | G. Deutscher et al. <u>Physical Review B</u> , vol. 21   |            |
|   |         | pp. 5041-5047, (1 June 1980).  |            |
|   | AG<br>1 | K. A. Muller et al. <u>Physical Review Letters</u> , vol. 45, pp. 832-835,   |            |
|   |         | (8 September 1980).  |            |
|   | AH<br>1 | R. A. Buhrman et al., in <u>AIP Conference Proceedings, Inhomogeneous Superconductors</u> - 1979, (Berkeley Springs, W.V.), D. U. Gubser et al.          |            |
|   |         | pp. 207-215 (1980).  |            |
|   | AJ<br>1 | T. D. Thanh et al. <u>Applied Physics</u> , vol. 22, pp. 205-212 (1980).   |            |
|   | AK<br>1 | C. Methfessel and S. Methfessel, in <u>Proceedings of the IV Conference on Superconductivity in d- and f- Band Metals</u> , W. Buckel and W. Weber, eds. |            |
|   |         | (Kernforschungszentrum, Karlsruhe, 1982), pp. 393-399.   |            |
| EXAMINER  |         | DATE CONSIDERED  |            |
| *EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. |         |  |            |

|   |    |  |                          |
|---|----|--|--------------------------|
| LIST OF REFERENCES CITED BY APPLICANT<br>(Use several sheets if necessary)  |    | STTY. DOCKET NO.<br>YO987-074  | SERIAL NO.<br>07/053,307 |
|   |    | APPLICANT<br>J. Georg Bednorz and K. Alex Mueller                            |                          |
|   |    | FILING DATE<br>22 May 1987   | GROUP<br>115             |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |    |  |                          |
|   | AA | A. Baratoff et al., In Proceedings of the IV Conference on Superconductivity |                          |
|   | 2  | In d- and f- Band Metals, W. Buckel and W. Weber eds.,                       |                          |
|   |    | (Kernforschungszentrum, Karlsruhe, 1982) pg. 419.                            |                          |
|   | AC | J. Muller, Rep. Prog. Phys., vol. 43, pp. 642-687, (1980)                    |                          |
|   | 2  |  |                          |
|   | AD | M. Suzuki et al., Shinku, vol. 24, pp. 67-75, (1981). [in Japanese].         |                          |
|   | 2  |  |                          |
|   | AE | K. A. Muller et al., Physical Review Letters, vol. 47, pp. 138-142,          |                          |
|   | 2  | (13 July 1981).  |                          |
|   | AF | Y. Enomoto et al., Japanese Journal of Applied Physics, vol. 20,             |                          |
|   | 2  | pp. L661-L664, (September 1981).   |                          |
|   | AG | B. K. Chakraverty, Journal de Physique, vol. 42,                             |                          |
|   | 2  | pp. 1351-1356, (September 1981).   |                          |
|   | AH | L. Er-Rakho et al., Journal of Solid State Chemistry, vol. 37,               |                          |
|   | 2  | pp. 151-156, (1981).   |                          |
|   | AI | A. Baratoff and G. Binnig, Physica, vol. 108B, pp. 1335-1336, (1981).        |                          |
|   | 2  |  |                          |
|   | AJ | L. F. Mattheiss and D. R. Hamann, Physical Review B, vol. 26,                |                          |
|   | 2  | pp. 2686-2689, (1 September 1982).   |                          |
|   | AK | L. F. Mattheiss and D. R. Hamann, Physical Review B, vol. 28,                |                          |
|   | 2  | pp. 4227-4241, (15 October 1983).  |                          |
|   | AL | K.-H. Hock et al, Helvetica Physica Acta, vol. 56, pp. 237-243, (1983).      |                          |
|   | 2  |  |                          |
| EXAMINER  |    | DATE CONSIDERED  |                          |
| <p>*EXAMINER Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.</p> |    |  |                          |

|   |   |   |                                      |
|---|---|---|--------------------------------------|
| LIST OF REFERENCES CITED BY APPLICANT<br>(Use several sheets if necessary)  |   | APP. DOCKET NO.   | SERIAL NO.                           |
|   |   | YO987-074   | 07/053,307                           |
|   |   | APPLICANT   | J. Georg Bednorz and K. Alex Mueller |
|   |   | FILING DATE   | GROUP                                |
|   |   | 22 May 1987   | 115                                  |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |   |   |                                      |
| AA  | 3 | N. Nguyen et al., <u>Journal of the Physics and Chemistry of Solids</u> , vol. 44, pp. 389-400, (1983).                                   |                                      |
| AD  | 3 | D. R. Bowman and D. Stroud, <u>Physical Review Letters</u> , vol. 52, pp. 299-302, (23 January 1984).                                     |                                      |
| AC  | 3 | M. Tinkham et al., <u>Workshop on Problems in Superconductivity</u> , Copper Mountain, CO, pp. 12-22, (1984).                             |                                      |
| AD  | 3 | B. Batlogg, <u>Physica</u> , vol. 126B, pp. 275-279, (1984).  |                                      |
| AE  | 3 | C. Ebner and D. Stroud, <u>Physical Review B</u> , vol. 31, pp. 165-171, (1 January 1985).  |                                      |
| AF  | 3 | M. R. Harrison et al., <u>Philosophical Magazine B</u> , vol. 52, pp. 679-699, (1985).  |                                      |
| AG  | 3 | E. Stocker and J. Buttet, <u>Solid State Communications</u> , vol. 53, pp. 915-917, (1985).   |                                      |
| AH  | 3 | C. Van Haesendonck and Y. Bruynseraede, <u>Physical Review B</u> , vol. 33, pp. 1684-1690, (1 February 1986).                             |                                      |
| AI  | 3 | H. R. Ott, <u>Unconventional Superconductivity</u> , Zurich Physical Society Seminar, Zurich, (13 February 1986), [in German].            |                                      |
| AJ  | 3 | T. Ogushi and Y. Osono, <u>Applied Physics Letters</u> , vol. 48, pp. 1167-1168, (28 April 1986).   |                                      |
| AK  | 3 | S.-I. Uchida et al. "High $T_c$ Superconductivity of La-Ba-Cu Oxides", unpublished nine-page manuscript bearing date of 22 November 1986. |                                      |
| AL  | 3 | Asahi Shinbun, International Satellite Edition (London), 28 November 1986, (in Japanese with English translation).                        |                                      |
| EXAMINER  |   | DATE CONSIDERED   |                                      |
| <p>*EXAMINER Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.</p> |   |   |                                      |

|   |         |  |            |
|---|---------|--|------------|
| LIST OF REFERENCES CITED BY APPLICANT<br>(Use several sheets if necessary)  |         | APP. LOCAL NO.   | SERIAL NO. |
|   |         | YO987-074  | 07/053,307 |
|   |         | APPLICANT<br>J. Georg Bednorz and K. Alex Mueller  |            |
|   |         | FILED DATE   | GROUP      |
|   |         | 22 May 1987  | 115        |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |         |  |            |
|   | AA<br>4 | H. Takagi et al., "High- $T_c$ Superconductivity of La-Ba-Cu Oxides. II-<br>Specification of the Superconducting Phase", unpublished nine-page<br>manuscript bearing date of 8 December 1986.  |            |
|   | AD<br>4 | S.-I. Uchida et al., "High- $T_c$ Superconductivity of La-Ba-Cu Oxides. III-<br>Electrical Resistivity Measurement" unpublished nine-page manuscript<br>(page 7 missing) bearing date of 22 December 1986.   |            |
|   | AD<br>4 | K. Kishio et al., "New High Temperature Superconducting Oxides.<br>( $\text{La}_{1-x}\text{Sr}_x$ ) $_2\text{CuO}_{4-\delta}$ and ( $\text{La}_{1-x}\text{Ca}_x$ ) $_2\text{CuO}_{4-\delta}$ " unpublished four-page<br>manuscript bearing date of 22 December 1986. |            |
|   | AF<br>4 | C. W. Chu et al. "Superconductivity Above 52K in the La-Ba-Cu-O System"<br>unpublished fourteen-page manuscript bearing date of 30 December 1986.  |            |
|   | AG<br>4 | W. Sullivan, <u>New York Times</u> , 31 December 1986, page A1, cols. 2-3 and<br>A13, cols. 1-2.   |            |
|   | AH<br>4 | S.-I. Uchida et al., "High- $T_c$ Superconductivity of La-Ba(Sr)-Cu Oxides.<br>IV - Critical Magnetic Fields" unpublished ten-page manuscript bearing<br>date of 8 January 1987.   |            |
|   | AJ<br>4 | S. Kanbe et al., "Superconductivity and Lattice Parameters in<br>( $\text{La}_{1-x}\text{Sr}_x$ ) $_2\text{CuO}_{4-\delta}$ Solid Solution System" unpublished four-page<br>manuscript bearing date of 13 January 1987.  |            |
|   | AL      |  |            |
| EXAMINER  |         | DATE CONSIDERED  |            |
| *EXAMINER Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not<br>in conformance and not considered. Include copy of this form with next communication to applicant. |         |  |            |

|   |  |  |            |
|---|--|--|------------|
| LIST OF REFERENCES CITED BY APPLICANT<br>(Use several sheets if necessary)  |  | ATTY. DOCKET NO.   | SERIAL NO. |
|   |  | YO987-074  | 07/053,307 |
|   |  | APPLICANT  |            |
|   |  | J. Georg Bednorz and K. Alex Mueller   |            |
|   |  | FILING DATE  | GROUP      |
|   |  | 22 May 1987  | 115        |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |  |  |            |
| AA  |  | H. Takagi et al., "Influence of the Oxygen Deficiency on the Electrical  |            |
| 5   |  | Resistivity In High-T <sub>c</sub> Superconducting Oxides (LaBa) <sub>2</sub> CuO <sub>4-y</sub> , unpublished |            |
|   |  | eight-page manuscript bearing date of 17 January 1987..  |            |
| AC  |  | Z. Zhao et al., "High T <sub>c</sub> Superconductivity of Sr(Ba)La-Cu Oxides"                                  |            |
| 5   |  | unpublished eleven-page manuscript bearing date of 21 January 1987.  |            |
| AD  |  |  |            |
| AE  |  |  |            |
| AF  |  |  |            |
| AG  |  |  |            |
| AH  |  |  |            |
| AI  |  |  |            |
| AJ  |  |  |            |
| AK  |  |  |            |
| AL  |  |  |            |
| EXAMINER  |  | DATE CONSIDERED  |            |
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UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

07/05/87 05/22/87 REIMORZ

J. DAVID ELLETT  
JRM INTELLECTUAL PROPERTY LAW DEPT.  
P.O. BOX 218  
YORKTOWN HEIGHTS, NY 10598

BOYD, J

115

04/20/91

DUE 7/25/91

☒ This application has been examined ☒ Responsive to communication filed on 2/13/91 ☒ This action is made final.

A shortened statutory period for response to this action is set to expire 3 month(s), — days from the date of this letter.  
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

- |   |   |
|---|---|
| 1. <input type="checkbox"/> Notice of References Cited by Examiner, PTO-892.        | 2. <input type="checkbox"/> Notice re Patent Drawing, PTO-948.                  |
| 3. <input type="checkbox"/> Notice of Art Cited by Applicant, PTO-1449.             | 4. <input type="checkbox"/> Notice of Informal Patent Application, Form PTO-152 |
| 5. <input type="checkbox"/> Information on How to Effect Drawing Changes, PTO-1474. | 6. <input type="checkbox"/>   |

Part II SUMMARY OF ACTION

1. ☒ Claims 1-95 are pending in the application.  
Of the above, claims 12-26, 36-39, 55-59 + 64 are withdrawn from consideration.
2. ☐ Claims have been cancelled.
3. ☐ Claims are allowed.
4. ☒ Claims 1-11, 27-35, 40-54, 60-63 + 65-68 are rejected.
5. ☐ Claims are objected to.
6. ☐ Claims are subject to restriction or election requirement.
7. ☐ This application has been filed with informal drawings under 37 C.F.R. 1.85 which are acceptable for examination purposes.
8. ☐ Formal drawings are required in response to this Office action.
9. ☐ The corrected or substitute drawings have been received on \_\_\_\_\_. Under 37 C.F.R. 1.84 these drawings are ☐ acceptable; ☐ not acceptable (see explanation or Notice re Patent Drawing, PTO-948).
10. ☐ The proposed additional or substitute sheet(s) of drawings, filed on \_\_\_\_\_, has (have) been ☐ approved by the examiner; ☐ disapproved by the examiner (see explanation).
11. ☐ The proposed drawing correction, filed \_\_\_\_\_, has been ☐ approved; ☐ disapproved (see explanation).
12. ☐ Acknowledgement is made of the claim for priority under U.S.C. 119. The certified copy has ☐ been received ☐ not been received  
☐ been filed in parent application, serial no. \_\_\_\_\_; filed on \_\_\_\_\_.
13. ☐ Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.
14. ☐ Other

EXAMINER'S ACTION



1. Applicant's election with traverse of Group I in Paper No. 22 is acknowledged. The traversal is on the ground(s) that the claims of Groups I, II and III are not distinct. This is not found persuasive because the Examiner maintains that the superconductive product, process of making and method of use are directed to patentally distinct inventions. Although there are broad "process" and "method" claims that appear to encompass a great deal of subject matter, the limitations in the dependent claims distinguish the claims of the Groups I, II and III.

The requirement is still deemed proper and is therefore made FINAL.

2. The objection to the specification and objection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 112, first paragraph, is maintained.

3. The following is a quotation of the first paragraph of 35 U.S.C. § 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

4. The Applicants assert that "the scope of the claims as presently worded is reasonable and fully merited" (page 17 of

Art Unit 115

response). The Examiner disagrees. The present claims are broad enough to include a substantial number of inoperable compositions.

5. The rejection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 112, second paragraph is maintained.

6. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

7. The amended term "rare earth-like" is vague. With respect to the lack of stoichiometry, Applicants argue the superconductive properties can be measured as the composition is varied. This is unpersuasive because the present claims broad enough to require an undue amount of experimentation.

8. The Examiner maintains that the term "doping" is vague. Neither the claim or the specification discuss the limits of the effective amounts of doping.

9. The Applicants assert that a discussion of "electron-phonon interactions to produce superconductivity" is found in the specification. The Examiner maintains that the term is not adequately explained. The specification fails to teach how one determines how to enhance the "electron-phonon" interactions?

10. The term "at least four elements" is indefinite considering the number of elements in the periodic table.

Art Unit 115

11. The rejection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 102/103 is maintained.

12. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Shaplygin et.al., Nguyen et.al., Michel et.al. (Mat. Res. Bull. and Revue de Chimie).

13. The Applicants argue that "no prima facie case has been made that the composition anticipates or renders obvious the subject matter" (page 28 of response). The Examiner maintains that these materials appear to be identical to those presently claimed except that the superconductive properties are not disclosed. Applicants have not provided any evidence that the compositions of the cited references are in any way excluded by the language of the present claims, i.e. Applicants have failed to show that these materials are not superconductive. Applicant's composition claims do not appear to exclude these materials.

14. Applicants further argue that under United States patent law they are entitled to claim compositions which might happen to overlap a portion of the concentration ranges broadly recited in the cited references. "The broad statement of a concentration range in the prior art does not necessarily preclude later invention within the concentration range" (page 29 of response). The Examiner fails to understand how Applicant's incredibly broad claims, some of

Art Unit 115

which require only the presence of a "doped transition metal oxide" (see claim 42), in anyway fall "within" the scope of the compositions disclosed in the prior art. The cited references disclose very specific compositions that not only fall within the scope of the claims, but appear to be identical to those compositions disclosed in the specification as being superconducting. The Examiner maintains that these materials are inherently superconductive and therefore render the claim unpatentable.

15. With respect to Applicants arguments under 35 USC 103 regarding the "question of non-analogous art" and the assertion the cited prior art is irrevelant to the present claim, the Examiner maintains that for the present "composition" claims the references directed to what appear to be identical materials (both in composition and inherent properities) are clearly relevant. The cited individual disclosures appear to be sufficient to maintain the rejection, the Examiner is not relying on any secondary references to modify the teachings in the references.

16. The rejection of claims 1-2, 5-11, 40-44, 46, 48, 51-54, 60, 62 and 66 under 35 USC 102/103 is maintained.

17. Claims 1-2, 5-11, 40-44, 46, 48, 51-54, 60, 62 and 66 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Perron-

Serial No. 07/53,307

-6-

Art Unit 115

Simon et.al., Mossner et.al., Chincholkar et.al., Amad et.al., Blasse et.al., Kurihara et.al. and Anderton et.al.

18. This rejection is maintained for the reasons set forth in the previous paragraphs. The Examiner maintains that the cited references appear to disclose materials which inherently provide superconductive properties and therefore render the present claims unpatentable.

19. THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 C.F.R. § 1.136(a).

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS FINAL ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS ACTION. IN THE EVENT A FIRST RESPONSE IS FILED WITHIN TWO MONTHS OF THE MAILING DATE OF THIS FINAL ACTION AND THE ADVISORY ACTION IS NOT MAILED UNTIL AFTER THE END OF THE THREE-MONTH SHORTENED STATUTORY PERIOD, THEN THE SHORTENED STATUTORY PERIOD WILL EXPIRE ON THE DATE THE ADVISORY ACTION IS MAILED, AND ANY EXTENSION FEE PURSUANT TO 37 C.F.R. § 1.136(a) WILL BE CALCULATED FROM THE MAILING DATE OF THE ADVISORY ACTION. IN NO EVENT WILL THE STATUTORY PERIOD FOR RESPONSE EXPIRE LATER THAN SIX MONTHS FROM THE DATE OF THIS FINAL ACTION.

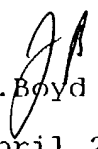
Any inquiry concerning this communication or earlier communications from the examiner should be directed to John Boyd whose telephone number is (703) 308-3314.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

Serial No. 07/53,307

-7-

Art Unit 115

  
J. Boyd

April 24, 1991

PAUL LIEBERMAN  
SUPERVISORY PRIMARY EXAMINER  
ART UNIT 115

Certificate of Mailing -- Date of Deposit: 8 February 1991  
Petition and Fee for Extension of Time (in triplicate)  
Amendment Transmittal Letter (in triplicate)  
Appointment of Associate Attorney  
Response to an Office Action  
Return PLEASE STAMP & RETURN TO US

Post Card.

in re application of: J. G. Bednierz and K.A. Mueller

For: New Superconductive Compounds Having High Temp.....

Serial No.: 07/053,307 Docket No.: YO987-074 Atty.: JDE

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification \_\_\_\_: No. of pages of claims \_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

Certificate of Mailing -- Date of Deposit: 8 February 1991  
Petition and Fee for Extension of Time (in triplicate)  
Amendment Transmittal Letter (in triplicate)  
Appointment of Associate Attorney  
Response to an Office Action  
Return PLEASE STAMP & RETURN TO US

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in re application of: J. G. Bednierz and K.A. Mueller

For: New Superconductive Compounds Having High Temp.....

Serial No.: 07/053,307 Docket No.: YO987-074 Atty.: JDE

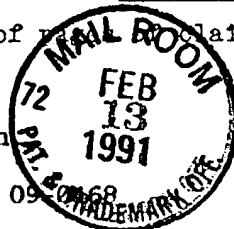
Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification \_\_\_\_: No. of pages of claims \_\_\_\_

No. of sheets of drawings: \_\_\_\_\_

Declaration is attached to specification

All fees are charged to our Account No. 09-0468



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J. Georg Bednorz and K. Alex Mueller

Serial No: 07/053,307

Group No: 115

Filed: 22 May 1987

Examiner: John Boyd

For: New Superconductive Compounds Having High Transition  
Temperature, and Methods for Their Use and Preparation  
Commissioner of Patents and Trademarks

Washington, D.C. 20231

CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)

I hereby certify that the *attached* correspondence comprising:

1. Amendment Transmittal Letter (in triplicate)
2. Petition and Fee for Extension of Time (in triplicate)
3. Appointment of Associate Attorney
4. Response to an Office Action
5. Return Post Card

is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

*Commissioner of Patents and Trademarks*

*Washington, D.C. 20231*

on 8 February 1991.

J. David Ellett, Jr. (Reg. 27,875)

(Type or print name of person mailing paper)

(Signature of person mailing paper)

DOCKET NO. YO987-074



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : Date: 8 February 1991  
J. Georg Bednorz and : Group Art Unit: 115  
K. Alex Mueller : Examiner: John Boyd  
Serial No.: 07/053,307 :  
Filed: 22 May 1987 : IBM Corporation  
For: NEW SUPERCONDUCTIVE : Intellectual Property Law Department  
COMPOUNDS HAVING HIGH : P.O. Box 218  
TRANSITION TEMPERATURE, AND : Yorktown Heights, N.Y. 10598  
METHODS FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

PETITION AND FEE FOR EXTENSION OF TIME (37 CFR 1.136(a))

1. This is a petition for an extension of the time to respond to the Office Letter mailed on 8 August 1990 for a period of three (3) months from 8 November 1990 to and including 8 February 1991.
2. Applicant is other than a small entity.
3. Extension:

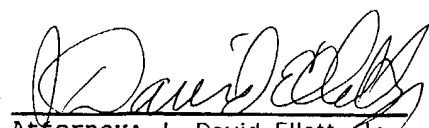
| <u>(months)</u>                                  | <u>Fee for other than<br/>small entity</u> |
|--|--|
| <input type="checkbox"/> one month               | \$ 100.00                                  |
| <input type="checkbox"/> two months              | \$ 300.00                                  |
| <input checked="" type="checkbox"/> three months | \$ <u>730.00</u>                           |
| <input type="checkbox"/> four months             | \$1150.00                                  |

Fee \$ 730.00

4. An amendment  
☒ is filed herewith  
☐ has been filed.
5. Fee payment  
☒ Charge fee to Deposit Account No. 09-0468 and for any additional extension fee required or credit for any excess fee paid. A duplicate of this petition is attached.

Respectfully submitted,

By

  
Attorney: J. David Ellett, Jr.  
Registration No.: 27,875

Docket No.: YO987-074

Telephone No.: (914) 241-4060

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

In re application of:  
J. Georg Bednorz and  
K. Alex Mueller

Date: 8 February 1991

Serial No.: 07/053,307

IBM CORPORATION  
INTELLECTUAL PROPERTY LAW DEPT.

Filed: 22 May 1987

P.O. Box 218

For: NEW SUPERCONDUCTIVE  
COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND  
METHODS FOR THEIR USE AND PREPARATION

Yorktown Heights, N.Y. 10598

THE COMMISSIONER OF PATENTS & TRADEMARKS  
WASHINGTON, D.C. 20231

Sir:

Transmitted herewith is an Amendment in the above-identified application.

☒ No additional fee is required.

☐ The fee has been calculated as shown below:

| (Col. 1)<br>CLAIMS<br>REMAINING<br>AFTER<br>AMENDMENT            |       | (Col. 2)<br>HIGHEST NO.<br>PREVIOUSLY<br>PAID FOR | (Col. 3)<br>PRESENT<br>EXTRA |
|--|-------|---|------------------------------|
| TOTAL 95   | MINUS | ** 95   | = 0                          |
| INDEP.   | MINUS | ***   | = 0                          |
| <input type="checkbox"/> 1ST PRESENTATION OF MULTIPLE DEP. CLAIM |       |   |                              |

| OTHER THAN A<br>SMALL ENTITY |               |
|------------------------------|---------------|
| RATE                         | ADDIT.<br>FEE |
| x 20 =                       | \$            |
| x 60 =                       | \$            |
| + 200 =                      | \$            |
| TOTAL                        | \$ 0.00       |

- \* If the entry in Col.1 is less than the entry in Col.2, write "0" in Col.3.  
 \*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, write "20" in this space.  
 \*\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, write "3" in this space.  
 The "Highest Number Previously Paid For" (Total or Independent) is the highest number found from the equivalent box in Col.1 of a prior amendment or the number of claims originally filed.

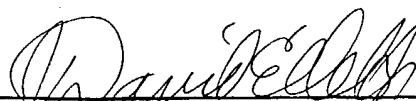
☐ Please charge my Deposit Account No. 09-0468 in the amount of \$\_\_\_\_\_. A DUPLICATE COPY OF THIS SHEET IS ENCLOSED.

☒ The Commissioner is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 09-0468. A DUPLICATE COPY OF THIS SHEET IS ENCLOSED.

☒ Any additional fees required under 37 CFR 1.16 for the presentation of extra claims.

☒ Any patent application processing fees under 37 CFR 1.17.

Respectfully submitted,

By: 

Attorney: J. David Ellett, Jr.  
Reg. No.: 27,875  
Telephone: (914) 241- 4060

Case Docket No.: YO987-074

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|                                     |   |                     |
|-------------------------------------|---|---------------------|
| In re Patent Application of         | : | Group Art Unit: 115 |
|                                     | : |                     |
| Applicant: J. GEORG BEDNORZ and     | : | Examiner: John Boyd |
| K. ALEX MUELLER                     | : |                     |
|                                     | : |                     |
| Serial No.: 07/053,307              | : |                     |
|                                     | : |                     |
| Filed: 22 May 1987                  | : |                     |
|                                     | : |                     |
| For: NEW SUPERCONDUCTIVE COMPOUNDS  | : |                     |
| HAVING HIGH TRANSITION TEMPERATURE, | : |                     |
| AND METHODS FOR THEIR USE AND       | : |                     |
| PREPARATION                         | : |                     |

RESPONSE TO AN OFFICE ACTION UNDER 37 CFR 1.111

Honorable Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

This is submitted in response to an Office Action issued on 8 August 1990 in connection with the patent application identified above. Pursuant to a petition for an extension of time submitted with this response, the time for response has been set for 8 February 1991.

A M E N D M E N T S

Please amend the subject application as set forth below.

In the Claims

Claim 1, line 3, delete "near."

Claim 32, line 3, for "composite" substitute -- composition --.

R E M A R K S

A. Summary of the Present Invention

The present invention broadly concerns a ceramic-like material which is superconductive with a superconductive/resistive transition temperature of about 26°K or greater. Preferred examples of such superconductive ceramic-like materials have a layer-like crystalline structure and an elemental composition of RE-AE-TM-O, where RE is a rare earth or rare earth-like element, AE is an alkaline earth element, TM is a transition metal element, and O is oxygen.

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B. Summary of the Outstanding Office Action

In the Office Action of 8 August 1990, restriction was required under 35 U.S.C. Section 121 to one of the following three groups of claims:

I. Claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65

through 68 inclusive, assertedly drawn to a superconducting composition, classified in Class 423, Subclass 604;

II. Claims 24 through 26 inclusive, 73 through 76 inclusive, 82, 83 and 86 through 90 inclusive, assertedly drawn to a method of making, classified in Class 505, Subclass 725; and

III. Claims 12 through 23 inclusive, 36 through 39 inclusive, 55 through 59 inclusive, 64, 69 through 72 inclusive, 77 through 81 inclusive, 84, 85, and 91 through 95 inclusive, assertedly drawn to a superconductor apparatus, classified in Class 505, Subclass 825.

It was asserted In the Office Action that the inventions of the claims of Group I and Group II were related as process of making and product made. It was asserted that such inventions would be distinct if (1) the processes claimed could be used to make other and materially different products, or (2) if the product as claimed could be made by another and materially different process. Section 806.05(f) of the Manual of Patent Examining Procedure ("the MPEP") was cited. It was asserted that in the instant case the product as claimed could be made by a process such as sputtering, which was characterized as materially different.

The inventions of the claims of Group I and Group III were asserted to be related as mutually exclusive species in an intermediate-final product relationship. It was asserted that distinctness would be established for claims in such a relationship if the intermediate product were useful to make other than the final product and the species were patentably distinct. Sections 806.04(b), third paragraph, and 806.04(h) of the MPEP were cited. It was asserted that, in the instant case, the intermediate product was deemed to be useful as a diamagnetic material used for bulk levitation. It was further asserted that the inventions were deemed patentably distinct since there was nothing in the present record to show the inventions to be obvious variants.

It was asserted in the Office Action that the inventions of the claims of Group II and Group III were related as process of making and product made. It was asserted that the inventions would be distinct if (1) the process claimed could be used to make another and materially different product, or (2) the product as claimed can be made by another and materially different process. Section 806.05(f) of the MPEP was cited. It was asserted that in the instant case the process could be used to make an assertedly materially different product such as a bulk diamagnetic material used for levitation.

It was asserted that because the inventions of Groups I, II, and III were distinct and had acquired a separate status in the art because of their assertedly recognized divergent subject matter, restriction for examination purposes was proper. It was stated that during a telephone conversation on 17 July 1990 with Mr. Jackson E. Stanland, an attorney for the applicants, a provisional election was made - with traverse - to prosecute the invention of Group I. It was indicated that affirmation of the provisional election must be made in the response to the outstanding Office Action. It was stated that claims 12 through 26 inclusive, 36 through 39 inclusive, 55 through 59 inclusive and 64 were withdrawn from further consideration as being drawn to a non-elected invention. The status of claims 69 through 95 inclusive was not indicated, although claims 69 through 95 had been assigned to the provisionally non-elected Groups II and III.

In the outstanding Office Action, the specification was objected to under 35 U.S.C. Section 112, first paragraph, as assertedly failing to provide an enabling disclosure commensurate with the scope of the claims. It was asserted that the subject specification was enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_y$ . It was asserted that the art of high temperature superconductors characterized as greater than 30°K - was unpredictable one. It was asserted that small changes in composition could result in dramatic changes in or loss of superconducting properties. It was stated that the amount and

type of examples necessary to support broad claims increased as the predictability of the art decreased. In re Fisher, 166 USPQ 18, 24 and In re Angstadt and Griffin, 190 USPQ 214, 218 were cited in this connection. It was asserted that claims broad enough to cover a large number of compositions that did not exhibit the desired properties failed to satisfy the requirements of 35 U.S.C. Section 112. In re Cook, 169 USPQ 244,262 was cited. It was stated that reciting a desired result did not overcome such asserted failure. In re Corkill, 266 USPQ 1005, 1009 was cited.

It was questioned whether any material containing copper would exhibit superconductivity. It was questioned whether CuO was a superconductor. It was questioned whether any stoichiometric combination of a rare earth, an alkaline earth, and copper was a superconductor. It was questioned whether  $Ce_{15}Mg_{0.05}Cu_{0.5}O_x$ ,  $Ba_xLa_{5-x}Ni_5O_y$ , and  $Mg_{10}Y_{0.05}Fe_{0.05}O_1$  were superconductors.

It was asserted that, at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. It was asserted that there was little factual or theoretical basis for extending the scope of the claims beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. Quoting Brenner v. Manson, 383 US 519, 148 USPQ 689, it was stated that a "patent is



not a hunting license. It is not a reward for the search, but a reward for its successful conclusion."

Claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive were rejected under 35 U.S.C. Section 112, first paragraph, with a reference to the objection to the specification.

In the outstanding Office Action, claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive were rejected under 35 U.S.C. Section 112, second paragraph, with the assertion that the claims were indefinite for assertedly failing to particularly point out and distinctly claim the subject matter which the applicants regarded as their invention.

The term "near rare earth-like element" was questioned. What elements this term excluded and included was questioned.

It was asserted that the rejected claims were indefinite insofar as each assertedly failed to recite any stoichiometric limitation. How the metes and bounds of the invention would be determined was questioned.

With respect to a recitation of "doping" in claim 11, it was questioned how much dopant was required.

The phrase "enhances electron-phonon interactions to produce superconductivity" was questioned.

It was stated that there was no antecedent basis for the term "composite" recited in claim 32.

It was stated that claim 62 recited an "oxygen excess." What the "excess" was in relation to and how it would be determined was questioned.

It was asserted that the term "transition temperature" was indefinite. It was questioned whether "transition temperature" corresponded to a temperature at which resistivity was zero or a temperature at which resistivity began to drop.

It was asserted that the term "said superconductor being comprised of at least four elements" recited in claim 40 was vague and indefinite. It was asked how one selected the elements and would any combination of four elements in any stoichiometric ratio produce the desired result.

It was noted in the Office Action that the subject application had been filed in the United States on 22 May 1987. Declarations to establish an earlier conception and reduction to practice date submitted for the present application by and on behalf of the inventors were acknowledged. Although it was

asserted in the Office Action that the exact date to which the applicants were entitled was not fully clear, it was asserted that such date appeared to have been no earlier than about 17 October 1986, a date on which a sample and enabling disclosure was brought to the United States from Switzerland by Praveen Chaudhari. The Declaration of Praveen Chaudhari was cited in this connection. It was asserted further that such date would appear to be no later than 13 December 1986, a date on which samples were tested in the United States to show superconductivity. The Declaration of Richard L. Greene was cited. It was indicated that no prior art of record disclosed La-Ba-Cu-O as a superconducting system prior to 1 January 1987 and that there was no need to make a judgement as to what date represented a reduction to practice. A number of publications having a filing date later than 1 January 1987 were cited for purposes of record. It was acknowledged that one of the publications, a publication by Ganguly and Rao in volume 97 of the Proceedings of the Indian Academy of Sciences which purported to have a publication date in December 1986, had to have been published later than 1 January 1987, since the publication cited other references which were not published until 1987.

In the outstanding Office Action, claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive were rejected under 35 U.S.C. Section 102(b) as anticipated by, or, in the alternative, under 35 U.S.C. Section 103 as assertedly obvious

over, each of a publication by Shaplygin et al. in the Russian Journal of Inorganic Chemistry, volume 24, pages 820-824 (1979) ("the Shaplygin et al. publication"); a publication by Nguyen et al. in the Journal of Solid State Chemistry, volume 39, pages 120-127 (1981) ("the Nguyen et al. publication"); a publication by Michel et al. in the Materials Research Bulletin, volume 20, pages 667-671 (1985) ("the 1985 Michel et al. publication"); and a publication by Michel and Raveau in the Revue de Chimie Minerale, volume 21, pages 407-425 (1984) ("the 1984 Michel and Raveau publication"). It was asserted that the Shaplygin et al. publication disclosed the composition  $\text{Ln}_{2-x}\text{M}_x\text{CuO}_4$ , where M was Ca, Sr, Ba and Pb and Ln was La, Pr, Nd, Sm, Eu, and Gd. It was asserted that  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_4$  was disclosed on page 823. It was asserted that the Nguyen et al. publication disclosed the composition  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ . It was asserted that 1984 Michel and Raveau publication disclosed the composition  $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_4$ , where A was Ca, Sr, Ba. It was further asserted that the 1985 Michel et al. publication disclosed the compositions  $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$  and  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+x}$ . Although it was conceded in effect in the Office Action that none of the four publications disclosed superconductivity, it was asserted that each of the four publications appeared to fall within the scope of the subject matter as presently claimed. It was asserted that the burden of proof was upon the applicants to show that the subject matter differed from and was unobvious over that disclosed in the publications. In re Brown, 173 USPQ 685, 688; In re Best, 195 USPQ

430 and In re Marosi, 218 USPQ 289, 293 were cited in this connection.

Claims 1, 2, 5 through 11 inclusive, 40 through 44 inclusive, 46, 48, 49, 51 through 54 inclusive, 60, 62, and 66 were rejected under 35 U.S.C. Section 102(b) as assertedly anticipated by, or, in the alternative, under 35 U.S.C. Section 103 as assertedly obvious over, each of the following: a publication by Perron-Simon et al. in C. R. Acad. Sc. Paris, volume 283, pages 33 through 35 (12 July 1976) ("the Perron-Simon et al. publication"); a publication by Mossner and Kemmler-Sack in the Journal of the Less-Common Metals, volume 105, pages 165 through 168 (1985) ("the Mossner and Kemmler-Sack publication"), a publication by Chincholkar and Vyawahare in Thermal Analysis 6th, volume 2, pages 251 through 256 (1980) ("the Chincholkar and Vyawahare publication"); a publication by Ahmad and Sanyal in Spectroscopy Letters, Volume 9, pages 39 through 55 (1976) ("the Ahmad and Sanyal publication"); a publication by Blasse and Corsmit in the Journal of Solid State Chemistry, volume 6, pages 513 through 518 (1973) ("the Blasse and Corsmit publication"); United States patent No. 3,472,779 to Kurihara et al. ("the Kurihara et al. '779 patent"); and a publication by Anderton and Sale in Powder Metallurgy No. 1, pages 14 through 21 (1979) ("the Anderton and Sale publication"). It was asserted that the Perron-Simon publication disclosed the composition  $\text{Ba}_2\text{La}(\text{Nb}_{13/3})\text{O}_{15}$ . It was asserted that the Mossner and Kemmler-Sack publication

disclosed the composition  $\text{Ba}_6\text{YNb}_{4.5}\text{O}_{18}$ . The Chincholkar and Vyawahare publication assertedly disclosed the composition  $\text{Ba}(\text{In}_{0.5}\text{B}_{0.5})\text{O}_3$ . It was asserted that the Ahmad and Sanyal publication disclosed  $\text{Ba}_2\text{YNbO}_6$  on page 43. It was asserted that the Blasse and Corsmit publication disclosed the composition  $\text{Ba}_2\text{GdNbO}_6$ . The Kurihara et al. '779 patent assertedly disclosed the composition  $\text{Ba}(\text{YNb})_{0.5}\text{O}_3$ . The Anderton and Sale publication assertedly disclosed the composition  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ . Although it was conceded in the Office Action that none of the references cited in this paragraph discussed superconductivity, it was asserted that each appeared to fall within the scope of the claims. It was asserted that a 1987 publication by Ogushi et al. in the Journal of Low Temperature Physics, volume 69, pages 451 through 457 (1987) ("the Ogushi et al. publication") disclosed that La-Sr-Nb-O systems were superconducting. Reference was made to the case law cited in the previous paragraph.

It was asserted in the outstanding Office Action that in the field of high temperature superconductors, many scientific developments were "available" as preprints prior to publication in a journal. It was further asserted that such a preprint was prior art as a printed publication under 35 U.S.C. Section 102(a) or (b) as of the date it was first distributed. The case 3M v. Ansul 213 USPQ 1024, 1037 was cited in this regard. It was requested that any information of the type noted above which was material to the subject matter presently claimed available prior

to the effective filing date of the present application of which the applicants were aware be promptly made of record.

It was suggested that any evidence to be presented in accordance with 37 C.F.R. 1.131 or 1.132 be submitted before final rejection to be considered timely.

C. Summary of the Present Amendments

Claim 1 has been amended to delete the term "near" from the expression "near rare earth-like element." The expression "rare earth-like element" conforms to the expression used in claim 2 as originally filed.

Claim 32 has been amended to correct a minor typographical or other clerical error. Specifically, the term -- composition -- has been substituted for the term "composite."

Reconsideration of the present application as amended and in the light of the comments below is respectfully requested.

D. The Restriction Requirement Under 35 U.S.C. Section 121

The applicants by their attorneys hereby affirm the previous provisional election to prosecute the invention of the claims denominated Group I in the Office Action of 8 August 1990

- specifically, claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive.

The requirement for restriction is respectfully traversed. It is submitted that the claims of Groups I, II and III are directed to inventions which are not "distinct" as that term is used for purposes of 35 U.S.C. Section 121, as explained below.

Turning first to the relationship between the subject matter of the claims of Group I and the claims of Group II, it is noted that - in contrast to the assertion in the Office Action - Group II is not limited to claims directed to a process of making. In addition to claims directed to a process of making a composition of the type which is the subject of claims of Group I, Group II includes claims directed to a method for using such a composition. See, for example, claims 24 through 26 inclusive and claims 86 through 90 inclusive. Furthermore, with regard to the assertion in the outstanding Office Action that the product as claimed in Group I could be made by a process such as sputtering, which is characterized as being materially different from the method for making claimed in Group II, it is submitted that such a sputtering process could well fall within the scope of one or more claims of Group II. See claim 75 in this regard, for example. For the reasons set forth above, it is submitted that the



inventions of the claims of Groups I and II are not distinct for restriction purposes. It is submitted therefore that the requirement of restriction between the claims of Groups I and II was unwarranted and should be withdrawn.

With respect to the relationship of the subject matter of the claims of Groups I and III, it was asserted that the so-called intermediate product of the claims of Group I would be useful as a diamagnetic material used for bulk levitation. However, it is submitted that levitation of superconductive diamagnetic material generally involves generating a magnetic field and immersing the material in the magnetic field. Immersing the superconductive diamagnetic material in such a magnetic field generally causes a supercurrent to be induced in the material which tends to oppose penetration of the magnetic field into the material, giving rise to the levitation effect. It is submitted that such a levitation system involving a diaelectric material of the claims of Group I would meet the limitations of one or more claims of Group II. Consider claim 12, for example. A magnet used to generate the magnetic field for such a levitation system would constitute means for passing a superconducting electrical current through the composition, as called for in claim 12. It is submitted, therefore, that the subject matter of the claims of Group I and III is not distinct for restriction-requirement purposes. It is thus submitted that the requirement for

restriction under 35 U.S.C. Section 121 between the claims of Groups I and III was not justified.

The comments in the preceding paragraphs regarding the subject matter of the claims of Groups II and III also apply with respect to the relationship between the subject matter of the claims of those two Groups. Specifically, it is noted again that not all of the claims of Group II are directed to a process of making, in contrast to the assertion in the outstanding Office Action. Furthermore, it is submitted that use of a process for making material to be employed as a bulk diamagnetic material for levitation would constitute a use which would fall within the scope of at least one of the claims of Group III - in contrast to an assertion in the outstanding Office Action. It is submitted, therefore, that the inventions of the claims of Group II and III are not distinct for restriction-requirement purposes and therefore that the requirement of restriction between the two groups in the Office Action was without justification.

In summary, for the reasons given above it is submitted that the requirement for restriction among the claims of Groups I, II and III in the outstanding Office Action was unwarranted and should be withdrawn.

E. The Rejection Under 35 U.S.C. Section 112, First Paragraph

The rejection under 35 U.S.C. Section 112, first paragraph, involves in one way or another the matter of the scope of the claims to which the present applicants are entitled. The Fisher case was cited in the outstanding Office Action in support of a contention that the applicants were not entitled to claims of the scope of the claims presently under examination. However, it is demonstrated below that if the advance in the art represented by the subject invention and the teachings of the subject application are properly taken into account as provided in the Fisher case, the doctrine of the Fisher case compels the conclusion that the scope of the claims as presently worded is reasonable and fully merited.

The court in the Fisher case analyzed the matter of the scope of patent protection to which an inventor was entitled in the following words:

The issue thus presented is whether an inventor who is the first to achieve a potency of greater than 1.0 for certain types of compositions, which potency was long desired because of its beneficial effect on humans, should be allowed to dominate all such compositions having potencies greater than 1.0, including future compositions having potencies far in excess of those obtainable from his teachings plus ordinary skill.

It is apparent that such an inventor should be allowed to dominate the future patentable inventions of others where those inventions were based in some way on his teachings. Such improvements, while unobvious from his teachings, are still within his contribution, since the improvement was made

possible by his work. It is equally apparent, however, that he must not be permitted to achieve this dominance by claims which are insufficiently supported and hence not in compliance with the first paragraph of 35 U.S.C. 112. That paragraph requires that the scope of the claims must bear a reasonable correlation to the scope of enablement provided by the specification to persons of ordinary skill in the art. In cases involving predictable factors, such as mechanical or electrical elements, a single embodiment provides board enablement in the sense that, once imagined, other embodiments can be made without difficulty and their performance characteristics predicted by resort to known scientific laws. In cases involving unpredictable factors, such as most chemical reactions and physiological activity, the scope of enablement obviously varies inversely with the degree of unpredictability of the factors involved.

Fisher 1009.

According to the court in the Fisher case, "the scope of the claims must bear a reasonable correlation to the scope of enablement provided by the specification to persons of ordinary skill in the art." Thus the standard against which the scope of claims is to be judged is the scope of enablement provided by the specification, not to persons in the abstract, but to persons of ordinary skill in the art. In the instant case, the scope of enablement provided by the specification to persons of ordinary skill in the art can readily be judged by the impact an article describing the invention had on such persons. Specifically, the present invention was disclosed in an article published by the present applicants in the Zeitschrift fur Physik - Condensed Matter in September 1986. The article is incorporated by reference in the specification of the instant application. Scientists throughout the world recognized the importance of the

invention and within only a few months of the publication had found numerous examples of the ceramic-like high temperature superconductors of the type disclosed in the article. Attached to this response as Exhibit A\* is a graph of the transition temperatures of the superconductive materials with the highest known transition temperatures versus the date of discovery of the superconductivity of such materials. As may be seen in Exhibit A, the rate of discovery of materials with higher temperatures increased dramatically in a short time after 1986, the date of publication of the Zeitschrift fur Physik article by the present applicants. It is submitted that whatever truth there may be to the generalization that chemical inventions tend to be less predictable than mechanical inventions, in the instant case, the evidence is plain that persons skilled in the relevant arts were able to build on the disclosure of the present invention as set forth in the Zeitschrift fur Physik article extremely productively and extremely rapidly relative to the rate of previous development in the field of superconductivity.

\*Exhibit A was taken from a report entitled "High Temperature Superconductivity: Perseverance and Cooperation on the Road to Commercialization" prepared under the auspices of the White House Science Council by the Committee to Advise the President on High Temperature Superconductivity. It should be noted the chairman and the executive secretary of the committee are or had been affiliated with the assignee of the instant application.

It is submitted therefore that under the doctrine of the Fisher case, the applicants are entitled to claims of the scope of the claims as presently worded, given the scope of enablement provided to persons of ordinary skill in this field by the specification of the subject application.

The Court of Customs and Patent Appeals has indicated that unpredictability of the relevant art is not the only factor to be considered in determining the breadth to which claims of a patent application are entitled. Specifically, a patent application is entitled to claims of broader scope to the extent that the application is directed to a pioneer invention. In re Hogan and Banks, 194 USPQ 527,537 (CCPA, 1977). As stated by the Court:

Rejections under [Section] 112, first paragraph, on the ground that the scope of enablement is not commensurate with the scope of the claims, orbit about the more fundamental question: To what scope of protection is this applicant's particular contribution to the art entitled?

Though we do not reach the point on this appeal, we note appellants' argument that their invention is of 'pioneer' status. The records reflects no citation of prior art disclosing a solid polymer of [the relevant monomer], which we may suggest that appellants at least broke new ground in a broad sense. On remand, appellants may be found to have been in fact the first to conceive and reduce to practice 'a solid polymer' as set forth in [the rejected claim on appeal]. As pioneers, if such they be, they would deserve broad claims to the broad concept. What were once referred

to as 'basic inventions' have led to 'basic patents,' which amounted to real incentives, not only to invention and its disclosure, but to its prompt, early disclosure.

Hogan and Banks, page 537. Thus in addition to considering the degree of unpredictability of the art, the advance the claimed invention has made over the prior art must be evaluated in determining the scope to which the claims are entitled.

In the instant case, the advance of the invention was of such a significant and pioneering nature that the inventors were awarded the Nobel Prize for Physics in 1987.

In response to the assertion in the outstanding Office Action that a claim which is so broad as to cover a large number of compositions which do not exhibit the desired properties fails to satisfy the requirements of 35 U.S.C. Section 112, it is noted that each of the composition claims of the subject application includes an express limitation with respect to desired superconductivity properties. Claim 1 of the application, for example, is directed to "a superconductive composition having a transition temperature greater than 26°K." Each of claims 2 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive includes directly or by reference analogous language with respect to superconductive properties.

With a citation to the Corkill case, it was asserted in effect in the outstanding Office Action that reciting a desired result in a claim does not remedy the problem of the claim's covering a large number of compositions which do not exhibit the desired result. The attorneys for the applicants, however, respectfully submit that the Corkill case does not support this proposition. In the Corkill case, the court affirmed a rejection under 35 U.S.C. Section 112, second paragraph, of certain claims in a continuation application under review which were drawn to a detergent composition. According to declarations submitted on behalf of the applicants, the rejected claims read on certain detergent compositions which led to "unacceptable deposition on clothing and washing machine surfaces." The specific claims in question were not set out in the decision in the Corkill case. However, a representative claim of a parent application of the continuation application made no mention of the desired result of avoiding deposition on clothing and washing machine surfaces. On page 1008, right hand column, last full sentence, the court stated that the only difference between the claims of the parent application and the continuation application was an upper limit on the size of certain particles in the detergent composition. In any event, the court made no reference to any recitation of a desired result in the rejected claims of the continuation application, nor did it state that such a recitation would be futile. It is would appear therefore that the Corkill case does not support the proposition that recitation of a desired result



somehow does not serve to exclude compositions which do not achieve the recited desired result.

In the instant case, the property of superconductivity is a physically measurable property of the composition being claimed. That the property is also useful and hence desirable should not exclude the property from serving to define the claimed composition. It is submitted that the recitations in the composition claims under rejection regarding superconductive properties serve to exclude compositions which do not have the required superconductive properties.

For the reasons given above, it is submitted that claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive are fully supported by an enabling disclosure and that the scope of such claims is reasonably correlated with the scope of enablement provided by the specification to those of ordinary skill in the art and is merited by the revolutionary advance in the art represented by the invention of the claims. It is submitted therefore that the rejection of claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive under 35 U.S.C. Section 112, first paragraph, was unjustified and should be withdrawn.

G. The Rejections Under 35 USC Section 112, Second Paragraph

The comments in the outstanding Office Action in connection with the rejection under 35 U.S.C. Section 112, Second Paragraph, will be considered in turn.

Although it is submitted that the term expression "near rare earth-like element" questioned in the outstanding Office Action is completely clear and would be understood by a person of even only ordinary skill in the art, claim 1 has been amended to delete the term "near" from the expression. The terminology in claim 1 as amended and claim 2 is consistent. The expression "rare earth-like element" is discussed, for example, on page 7, lines 8 through 12 in the application as originally filed.

With regard to the comment in the Office Action relating to the recitation of a stoichiometric limitation in the composition claims, the attorneys for the applicants point out that each of the claims in question includes a language specifying that the composition be superconductive with a transition temperature of greater than 26° K, or generally analogous language. The properties of superconductivity and the transition temperature are physical properties of a material which can be measured as certainly as the chemical composition of the material can be measured. It is submitted that a claim directed to composition defined in part by superconductivity properties is not

indefinite. The metes and bounds of the invention are defined with the particularity and distinctness required by the second paragraph of 35 U.S.C. Section 112 in each of the composition claims of the present invention.

With respect to the recitation of doping in claim 11, the specification provides a discussion of such doping on page 17, line 12 through page 19, line 12. Moreover, claim 11 depends upon claim 1 and thus incorporates the limitations of claim 1 by reference. It is submitted that claim 11, as presently worded, would be completely clear and definite to one of ordinary skill in the art, particularly in light of the discussion in the specification and in view of the limitations of claim 1 incorporated by reference.

Claim 31 of the present application is a dependent claim which depends upon independent claim 27. Claim 31 states that the claimed composition "has a crystalline structure which enhances electron-phonon interactions to produce superconductivity at a temperature in excess of 26°K." Electron-phonon interactions favorable to the occurrence of superconductivity at higher critical temperatures is discussed in the specification, for example, on page 15, line 20 through page 14, line 9. It is submitted that claim 31 incorporating the limitations of claim 27 upon which it depends and when read in the light of the specification is completely clear and definite.

Claim 32 has been amended to delete the term "composite" questioned in the outstanding Office Action. As amended, claim 32 refers to a composition for which there is an antecedent basis.

The term "oxygen excess" referred to in claim 62 refers to an excess of the oxygen content over a stoichiometric amount. See, for example, the discussion on page 27, line 13 through page 28, line 5 of the application as filed. It is submitted that the reference to oxygen excess would be understood by one of ordinary skill in the art and that claim 62 as presently worded is clear and definite.

The term "transition temperature" questioned in the outstanding Office Action refers to the transition in superconductive materials between a resistive state and the superconducting state. As used in the present application, the term is consistent with conventional usage. The transition temperature does not conventionally refer to the low temperature end of the transition, i.e. the temperature at which zero resistivity is achieved, but rather conventionally refers to a point in the transition from a resistive state to the superconducting state.

With respect to selection of "at least four elements" recited in claim 40, reference is made to the specification of the application which provides examples of superconductive

compositions comprising at least four elements. See, for example, page 12, lines 4 through 19 of the application. Claim 40 does not state or imply that any four elements in the periodic table in any stoichiometric ratio will result in a superconductor which exhibits a superconducting onset at a temperature in excess of 26° K. Claim 40 is directed to a superconductor which exhibits a superconducting onset at a temperature in excess of 26° K which is comprised of at least four elements, none of which itself is superconducting. That such superconductors exist was discovered by the present applicants and constitutes an invention which, it is submitted, they are entitled to claim.

For the reasons set forth above, it is submitted that the claims of the present application, as amended, meet the standards of 35 U.S.C. Section 112, second paragraph. The rejection of claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive under 35 U.S.C. Section 112, second paragraph, was without foundation and should be withdrawn.

H. The Rejections Under 35 U.S.C. Section 102(b)

It was conceded in the outstanding Office Action that none of the eleven references cited against the claims under examination discussed superconductivity. None of the references disclosed or in any way suggested that any composition disclosed

in the reference was superconductive at any temperature, let alone that the composition had a superconductive transition temperature of 26°K or greater.

The position taken in the Office Action was that even if a cited reference did not disclose or suggest that a composition disclosed in the reference was superconductive, the burden was upon the applicants to establish that the composition was not within the scope of the claims.

It is the position of the attorneys for the applicants that the comments in the outstanding Office Action do not so much as make out a prima facie case that any of the specific compositions disclosed in the cited references falls within the scope of any of the claims of the subject application. Absent some showing that one of the specific compositions disclosed in one of the eleven references is a material which is superconductive with a transition temperature of 26°K or greater, no prima facie case has been made that the composition anticipates or renders obvious the subject matter of a claim of the subject application.

Four of the references cited in the outstanding Office Action disclosed materials in terms of compositions which could vary over specified ranges. Specifically, the Shaplygin et al. publication, the Nguyen et al. publication, the 1984 Michel and Raveau publication and the 1985 Michel et al. publication each

disclosed certain compositions in which it was specified that one or more of the elements of the compensation could vary over a certain range.

However, under United States patent law, the applicants are fully entitled under 35 U.S.C. Section 102 to claim compositions which might happen to overlap a portion of the concentration ranges broadly recited in the Shaplygin et al., Nguyen et al, Michel and Raveau and Michel et al. publications, because they have discovered that the subject matter claimed has remarkable high-temperature superconductive properties totally unexpected in view of the publications.

The broad statement of a concentration range in the prior art does not necessarily preclude later invention within the concentration range. Whether or not a material subsequently discovered falling within the concentration range is patentable depends upon what the prior art teaches people skilled in the art about the properties of substances falling within that range; if the properties of the newly discovered material are unobvious in view of what the prior art teaches, it may be patentable. In re Waymouth and Koury, 182 USPQ (CCPA 1974). Thus "ranges which overlap or lie inside ranges disclosed by the prior art may be patentable if the applicant can show criticality in the claimed range by evidence of unexpected results." In re Wertheim 191 USPQ 90, 100 (CCPA 1976).

A case decided by the Court of Customs and Patent Appeals, In re Waymouth and Koury, 182 USPQ 290 (CCPA 1974), provides an example of a critical difference which supported patentability of subject matter falling within a range broadly disclosed in a prior-art patent.

The claims at issue in the Waymouth case related to high-pressure electric discharge lamps of a type used for outdoor lighting. The lamps included an arc tube which contains mercury and halogen atoms. Conventional high pressure electric discharge lamps emitted a bluish light, which was a drawback. The appellants found that maximum white light emissions could be achieved when the ratio of halogen atoms to mercury atoms was restricted to certain values. The claims at issue recited a range for the ratio of from about 0.08 to 0.75. Reference to Fig. 2 of the Waymouth and Koury application, which was reproduced in the opinion of the court, will show that the recited range for the ratio of halogen atoms to mercury atoms limited the intensity of white light emission to no less than approximately 0.5 of its highest value.

The claims on appeal had been rejected as unpatentable over an issued United States patent to Reiling. According to the court,

The Reiling patent discloses a device similar to that of appellants' and also seeks to produce white light. The Reiling device incorporates the halogen and mercury atoms used by appellants; however, the claimed ratio is not specifically disclosed in the reference. Appellants have calculated the ratios of halogen to mercury atoms inherently disclosed by



Reiling, which ratios span the range from 0.0000001 to 1.3. These ratios have not been contradicted by the board of solicitor.

Observe that over fifty percent of the range inherently disclosed by Reiling was claimed by the appellants.

In spite of the overlap between the claimed range and the range inherently disclosed in the Reiling patent, the court found that the claims were patentable over Reiling. The court based its decision in part on a finding that the claimed range of ratios was critical for the attainment of maximum white light emission. In the words of the court:

Although Reiling's range of possible ratios envelops the range claimed by appellants, we believe that the appellants' graph in Figure 2 demonstrates the necessary unexpected results. Those results follow from the selection of appellants' critical range, which is narrower than the extremely broad inherently disclosed range of Reiling. We cannot agree with the board's holding that since appellants' lamp is also operable over other ranges of the halogen atom to mercury atom ratio, Figure 2 does not demonstrate an unexpected result. In order to show an unexpected result, we do not believe that the lamp must be inoperable over other ranges, but rather that over the claimed critical range there be a difference in kind, rather than a degree. We believe that Figure 2 demonstrates such a marked improvement, over the results achieved under other ratios, as to be classified as a difference in kind, rather than one of degree. [Citations omitted.]

The discussion concerning criticality in the Waymouth case applies directly to the question of the criticality of the difference between the subject matter of the claims under discussion in the present application and the disclosures of the

Shaplygin et al., Nguyen et al., Michel and Raveau and Michel et al. publications. It is submitted, therefore, that the reasoning of the court in the Waymouth case compels a finding that the present invention represents a critical, and hence patentable, advance over the disclosures of the four publications.

A second case, In re Duva, 156 USPQ 90 (CCPA, 1967), like the Waymouth case, compels a finding that the claims under discussion are patentable over the Shaplygin et al., Nguyen et al., Michel and Raveau and Michel et al. publications. In the following discussion, the page, column, and line numbers refer to the opinion in the Duva case as reported in 156 USPQ.

The invention in the Duva case concerned a process for the "electroless" deposition of gold on a metal article immersed in a chemical solution. Since gold was deposited by direct chemical action, the process did not require electrodes or a source of electric current as did conventional electroplating processes. The two claims specifically analyzed by the court were directed to "a process for depositing gold on a workpiece" and to the chemical solution used in the process. The two claims had been rejected under 35 U.S.C. Section 103 as unpatentable over a reference which disclosed a process for the electrodeposition of a gold-palladium alloy and an electroplating bath for use in the process. The claim directed to the solution is reproduced below with paragraphing and lettering added for convenience.

1. As a composition for chemically depositing gold and aqueous solution consisting essentially of:

- (a) 0.5-30 g/l of a soluble gold cyanide,
- (b) 0.01 to 30 g/l of a soluble palladous salt,
- (c) absent sufficient CN ions to prevent deposition induced by said palladous salt, and
- (d) sufficient alkali to provide a pH of 8-11.

It is clear from the opinion in the Duva case that the concentration ranges to which the claims on appeal were directed overlapped to concentrations of the prior-art electroplating bath. The court pointed out that the examiner had noted that the proportions of gold cyanide and palladium salt in the claims "overlapped" those of the prior-art electroplating bath. Page 92, column 2, lines 25-28. In addition, the claims called for "sufficient alkali to provide a pH of 8-11," which overlapped with a teaching in the prior-art reference that the electroplating bath preferably have a pH of between 10 and 10.5. Page 92, column 2, lines 16-19. Finally, there was an overlap between the concentration range of cyanide ions called for in the claims and the concentration range of cyanide ions disclosed in the prior-art reference. The reference disclosed a single specific example of an electroplating bath. Page 92, column 2, footnote 6. In addition to the compound gold cyanide, the bath included four base-metal cyanide compounds in specified proportions. The reference further stated that the concentrations of the example could be increased up to three times the quantities recited. However, the patent also stated that the base-metal cyanide compounds were optional and that one or more base metals could be omitted. Page 93, column 1, lines 7-16. Were all four of the

base-metal cyanide compounds to be omitted from the electroplating bath, for example, the cyanide-ion concentration of the resulting bath would overlap the concentrations specified in the claims at issue. In part for this reason the Board of Appeals stated that it did not accord patentable distinction to the limitations in the claims relating to cyanide content and upheld the rejection. Page 93, column 1, lines 20-23.

The Court of Customs and Patent Appeals reversed the decision of the Board of Appeals in spite of the overlap of concentrations. Concerning the cyanide-ion concentration, the court held:

The prior art reference evinces no criticality about the concentration of the cyanide ions whereas appellant's invention depends upon using 'a soluble palladous salt, absent sufficient CN ions to prevent deposition induced' by the palladous salt.

Appellant asserts there is a critical aspect to his invention concerning the concentration of cyanide ions in the bath composition. The solicitor, however, urges that the amount of potassium cyanide used in the prior art reference satisfied the 'broad language' of the claims before the court. We do not agree with this position. When fairly considered for what it teaches one of ordinary skill in the art, the prior art patent does not make obvious the cyanide limitations present in the appealed claims.

Page 94, column 2, lines 17-37. Thus, by looking at the invention as a whole, the court recognized a patentable distinction with respect to the cyanide-ion limitations in the claims at issue, even though these limitations permitted an overlap with the cyanide-ion concentration disclosed in the prior art. It is

important to recognize that the court reached its decision by comparing the claimed subject matter as a whole with the teachings of the prior-art reference, taken for what it fairly taught people of ordinary skill in the art. The existence of an overlap in concentrations did not preclude such an analysis.

Turning now to the compositions of the claims under examination, it is submitted that the superconductive properties of the compositions of the claims represent a critical distinction over the properties disclosed for the compositions of the Shaplygin et al., Nguyen et al., Michel and Raveau and Michel et al. publications. Consequently, the compositions of the claims are patentable under the doctrine of the Waymouth and Duva cases over the four publications whether or not an overlap might exist between a claimed composition and a range of compositions disclosed in one of the Shaplygin et al., Nguyen et al., Michel and Raveau and Michel et al. publications.

For the reasons set forth above, it is submitted that the subject matter of claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive of the subject application is not anticipated by any of the eleven references cited in the outstanding Office Action. The rejections of the claims just recited under 35 U.S.C. Section 102(b) as unpatentable over the Shaplygin et al. publication, the Nguyen et al. publication, the

Michel and Raveau publication and the Michel et al. publication and the rejections of claims 1, 2, 5 through 11 inclusive, 40 through 44 inclusive, 46, 48, 49, 51 through 54 inclusive, 60, 62 and 66 under 35 U.S.C. Section 102(b) as unpatentable over the Perron-Simon et al. publication, the Mossner and Kemmler-Sack publication, the Chincholkar and Vyawahare publication, the Ahmad and Sanyal publication, the Blasse and Corsmit publication, the Kurihara et al, '779 patent and the Anderton and Sale publication were unjustified and should be withdrawn.

I. The Rejections Under 35 USC Section 103

It was conceded in the outstanding Office Action that none of the prior art references cited in connection with the rejection under 35 U.S.C. Section 103 disclosed superconductivity. It is submitted, therefore, that all of the patents and publications in question are non-analogous art and therefore not relevant to an analysis the subject matter claimed in the present application under 35 U.S.C. Section 103. A two-fold test for determining whether a reference is from a non-analogous art was stated in In re Deminski 230 USPQ 313, 315 (Fed. Cir. 1986). Under the Deminski test, it must first be determined whether or not the reference in question is within the field of the inventor's endeavor. If it is not, then it must be determined whether the reference is reasonably pertinent to the particular problem with which the inventor was involved.

With respect to the eleven references cited against the present claims in the outstanding Office Action, inasmuch as none of the references mentioned superconductivity, none was within the field of the endeavor of the inventors. Moreover, there is nothing to suggest that any of the eleven cited references was in any way pertinent to the problem of searching for a high-Tc superconductor. Specifically, no prior art patent or publication was cited in the outstanding Office Action which would have suggested that any of the materials disclosed in any of the cited references might be superconductive at any temperature, let alone at temperatures in excess of 26°K. Under the Deminski test, therefore, each of the eleven references cited in connection with the rejections under 35 U.S.C. Section 103 represents non-analogous and may not be used to establish obviousness of the claimed invention.

For the reasons set forth above, it is submitted that the composition of claims 1 through 11 inclusive, 27 through 35 inclusive, 40 through 54 inclusive, 60 through 63 inclusive, and 65 through 68 inclusive were neither disclosed nor suggested by the eleven cited references, taken either alone or in any combination. The rejection of the claims under 35 U.S.C. Section 103 as unpatentable over the references was unjustified and should be withdrawn.

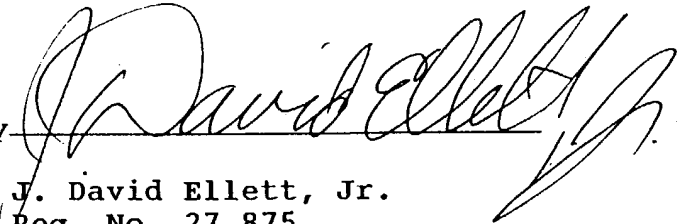
J. Conclusion

It is submitted that the subject matter of the claims of the present application as amended is neither disclosed nor suggested by the art of record considered singly or in any combination and that the claims of the application meet the standards of 35 U.S.C. Section 112, first and second paragraph. Early allowance of the application is therefore earnestly requested.

Respectfully submitted,

Attorneys for the Applicants

by



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8 February 1991



# **High Temperature Superconductivity: Perseverance and Cooperation on the Road to Commercialization**

by

**The Committee to Advise the President  
on High Temperature Superconductivity**

(Under the Auspices of The White House Science Council)

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The members of the advisory committee are:

R.E. Gomory — Chairman  
P. Chaudhari — Executive Secretary  
H.K. Bowen  
J.S. Foster  
T.H. Geballe  
M.K. Oshman  
J.R. Schrieffer

The advisory committee was ably assisted in organizing, in writing and in scheduling its meetings by Dr. A.H. Nethercot and Ms. Lorraine Miro.

# CHAPTERS OF THE REPORT

## 1. Introduction

Since the remarkable discovery by G. Bednorz and K.A. Müller (in the Swiss laboratory of a U.S. corporation) of superconductivity at temperatures as high as 40K, there has been an explosive growth in the amount of research done and in the number of important new results found in this field. Prior to this discovery, it was generally believed that it was unlikely for the transition to the superconducting state to occur at temperatures much higher than 30K. Today, it is not possible to predict what the ultimate temperature limit to superconductivity may be. The rapid pace of recent developments and the previous history of superconducting transition temperatures stretching over the past seventy-seven years are shown in Fig. 1.

Rarely before have so many disciplines come together in such a short time in so many countries to work on one scientific and technological subject. Physicists, chemists, ceramists and metallurgists, frequently working together, are involved in understanding and controlling the properties of these complex materials.

This research is being carried out at industrial, university and government laboratories in the U.S., Europe and Japan. Furthermore, both major recognized groups as well as recently instituted smaller groups with

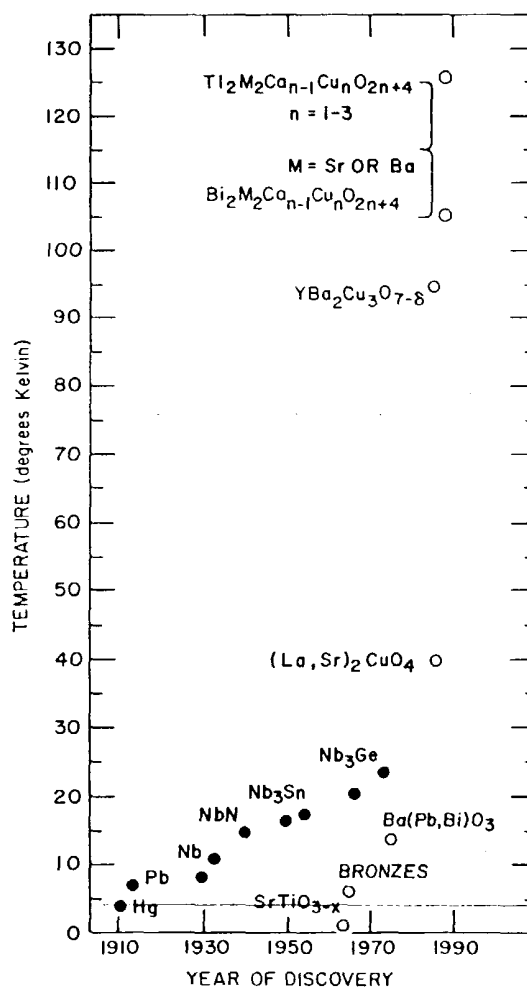


FIG. 1

ideas and with initiative are playing important roles. An entirely new information network has grown up in this area and operates in parallel with conventional research publication procedures: a very active and organized distribution of pre-publication results is occurring which has greatly hastened the pace of progress.

This worldwide interest in superconductivity is intense. The two most prominent countries in terms of research results are the United States and Japan, but the USSR, France, W. Germany, China, and India also have made significant contributions and even smaller countries such as Portugal and Hungary are publishing results. At a recent international conference held in Europe there were over 800 papers authored by scientists from 39 countries.

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|                                     |   |                     |
|-------------------------------------|---|---------------------|
| In re Patent Application of         | : | Group Art Unit: 115 |
|                                     | : |                     |
| Applicant: J. GEORG BEDNORZ and     | : | Examiner: John Boyd |
| K. ALEX MUELLER                     | : |                     |
|                                     | : |                     |
| Serial No.: 07/053,307              | : |                     |
|                                     | : |                     |
| Filed: 22 May 1987                  | : |                     |
|                                     | : |                     |
| For: NEW SUPERCONDUCTIVE COMPOUNDS  | : |                     |
| HAVING HIGH TRANSITION TEMPERATURE, | : |                     |
| AND METHODS FOR THEIR USE AND       | : |                     |
| PREPARATION                         | : |                     |

APPOINTMENT OF ASSOCIATE ATTORNEY

Honorable Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

The undersigned attorney, who has been appointed as an attorney in the Declaration and Power of Attorney for the patent application identified above, hereby appoints J. David Ellett, Jr. (Registration No. 27,875) of IBM Corporation, Intellectual Property Law Department, Post Office Box 218, Yorktown Heights, New York 10598, telephone number (914) 241-4060, his associate attorney to prosecute the application and to transact all business in the Patent and Trademark Office in connection therewith.

Please direct all official communications to  
J. David Ellett, Jr. at the address noted above.

Respectfully submitted,

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8 February 1991

**Patent and Trademark Office**Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

|               |             |                      |                   |
|---------------|-------------|----------------------|-------------------|
| SERIAL NUMBER | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET # |
| 07/053,307    | 05/22/87    | BEDNORZ              | J Y0987-074       |

JACKSON E. STANLAND  
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P.O. BOX 218  
YORKTOWN HEIGHTS, NY 10598EXAMINER  
BOYD, JART UNIT  
115

DATE MAILED: 08/08/90

This is a communication from the examiner in charge of your application.  
COMMISSIONER OF PATENTS AND TRADEMARKS

DUE 11/8/90

☒ This application has been examined ☐ Responsive to communication filed on \_\_\_\_\_ ☐ This action is made final.A shortened statutory period for response to this action is set to expire 3 month(s), \_\_\_\_\_ days from the date of this letter.  
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133**Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:**

- |   |   |
|---|---|
| 1. <input checked="" type="checkbox"/> Notice of References Cited by Examiner, PTO-892. | 2. <input type="checkbox"/> Notice re Patent Drawing, PTO-948.                  |
| 3. <input checked="" type="checkbox"/> Notice of Art Cited by Applicant, PTO-1449.      | 4. <input type="checkbox"/> Notice of Informal Patent Application, Form PTO-152 |
| 5. <input type="checkbox"/> Information on How to Effect Drawing Changes, PTO-1474.     | 6. <input type="checkbox"/> _____   |

**Part II SUMMARY OF ACTION**

1. ☒ Claims 1-95 are pending in the application.  
Of the above, claims 12-26, 30-39, 55-59, 164 are withdrawn from consideration.
2. ☐ Claims \_\_\_\_\_ have been cancelled.
3. ☐ Claims \_\_\_\_\_ are allowed.
4. ☒ Claims 1-11, 17-35, 40-54, 60-63, 165-168 are rejected. IBM  
YORKTOWN  
NY
5. ☐ Claims \_\_\_\_\_ are objected to.
6. ☐ Claims \_\_\_\_\_ are subject to restriction or election requirement.
7. ☐ This application has been filed with informal drawings under 37 C.F.R. 1.85 which are acceptable for examination purposes.
8. ☐ Formal drawings are required in response to this Office action.
9. ☐ The corrected or substitute drawings have been received on \_\_\_\_\_. Under 37 C.F.R. 1.84 these drawings are ☐ acceptable; ☐ not acceptable (see explanation or Notice re Patent Drawing, PTO-948).
10. ☐ The proposed additional or substitute sheet(s) of drawings, filed on \_\_\_\_\_, has (have) been ☐ approved by the examiner; ☐ disapproved by the examiner (see explanation).
11. ☐ The proposed drawing correction, filed \_\_\_\_\_, has been ☐ approved; ☐ disapproved (see explanation).
12. ☐ Acknowledgement is made of the claim for priority under U.S.C. 119. The certified copy has ☐ been received ☐ not been received  
☐ been filed in parent application, serial no. \_\_\_\_\_; filed on \_\_\_\_\_.
13. ☐ Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.
14. ☐ Other

EXAMINER'S ACTION

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1. Restriction to one of the following inventions is required under 35 U.S.C. § 121:

I. Claims 1-11, 27-35, 40-54, 60-63, and 65-68, drawn to a superconducting composition, classified in Class 423, subclass 604.

II. Claims 24-26, 73-76, 82-83 and 86-90, drawn to a method of making a method of making, classified in Class 505, subclass 725.

2. III. Claims 12-23, 36-39, 55-59, 64, 69-72, 77-81, 84-85 and 91-95, drawn to a superconductor apparatus, classified in Class 505, subclass 825.

3. The inventions are distinct, each from the other because of the following reasons:

Inventions I and II are related as process of making and product made. The inventions are distinct if either or both of the following can be shown: (1) that the process as claimed can be used to make other and materially different product or (2) that the product as claimed can be made by another and materially different process (M.P.E.P. § 806.05(f)). In the instant case the product as claimed can be made by a materially different process such as sputtering.

4. Inventions I and III are related as mutually exclusive species in intermediate-final product relationship. Distinctness is proven for claims in this relationship if the intermediate



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product is useful to make other than the final product (M.P.E.P. § 806.04(b), 3rd paragraph), and the species are patentably distinct (M.P.E.P. § 806.04(h)).

In the instant case, the intermediate product is deemed to be useful as a diamagnetic material used for bulk levitation and the inventions are deemed patentably distinct since there is nothing on this record to show them to be obvious variants. Should applicant traverse on the ground that the species are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the species to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the inventions anticipated by the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. § 103 of the other invention.

5. Inventions II and III are related as process of making and product made. The inventions are distinct if either or both of the following can be shown: (1) that the process as claimed can be used to make other and materially different product or (2) that the product as claimed can be made by another and materially different process (M.P.E.P. § 806.05(f)). In the instant case the process can be used to make a materially different product such as a bulk diamagnetic material used for levitation.

6. Because these inventions are distinct for the reasons given above and have acquired a separate status in the art because of

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their recognized divergent subject matter restriction for examination purposes as indicated is proper.

7. During a telephone conversation with Mr. Jackson B. Stanland on July 17, 1990 a provisional election was made with traverse to prosecute the invention of I, claim s 1-11, 27-35, 40-54, 60-63 and 65-68. Affirmation of this election must be made by applicant in responding to this Office action. Claims 12-26, 36-39, 55-59 and 64 are withdrawn from further consideration by the Examiner, 37 C.F.R. § 1.142(b), as being drawn to a non-elected invention.

8. The following is a quotation of the first paragraph of 35 U.S.C. § 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims. The present s specification is enabled only for compositions comprising  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_y$ .

The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting

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properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases. See In re Fisher, 166 U.S.P.Q. 18, 24 and In re Angstadt and Griffin, 190 U.S.P.Q. 214, 218. Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 U.S.C. 112. See In re Cook, 169 U.S.P.Q. 244, 262. Merely reciting a desired result does not overcome this failure. In re Corkill, 226 U.S.P.Q. 1005, 1009. In particular, the examiner questions if any material containing copper will exhibit superconductivity? Is CuO a superconductor? Is any stoichiometric combination of a rare earth, an alkaline earth and copper a superconductor? Is  $\text{Ce}_{15}\text{Mg}_{0.05}\text{Cu}_{0.5}\text{O}_x$  a superconductor? Is  $\text{Ba}_x\text{La}_{5-x}\text{Ni}_5\text{O}_y$ ? Is  $\text{Mg}_{10}\text{Y}_{0.05}\text{Fe}_{0.05}\text{O}_1$ ? It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. (This is still the case today). Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity. A "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion", Brenner v. Manson, 383 U.S. 519, 148 U.S.P.Q. 689.

9. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected

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under 35 U.S.C. § 112, first paragraph, for the reasons set forth in the objection to the specification.

10. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

11. What does the term "near rare earth-like element" mean? What elements does this language exclude? What does it include?

12. These claims are indefinite as each fails to recite any stoichiometric limitation. How does one determine the metes and bounds of the present invention?

13. Claim 11 recites "doping". How much dopant is required? Will using 0.0001% produce the desired result?

14. What is meant by "enhances electron-phonon interactions to produce superconductivity"?

15. Claim 32 recites "in said composite". There is no antecedent basis for "composite"? In addition, composite implies a material made up of distinct components, such as a cermet. Is applicant claiming such a material?

16. Claim 62 recites an "oxygen excess"? What is this "excess" in relation to? How does one determine this?

17. The term "transition temperature" is indefinite. Does this term correspond to the temperature at which resistivity is zero? Or does it relate to the temperature at which the resistivity

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begins to drop? If the latter is true, at what temperature is zero resistivity reached?

18. claim 40 recites "said superconductor being comprised of at least four elements". This term is vague and indefinite. How does one select these elements? Will any combination of four elements in any stoichiometric ratio produce the desired result?

19. The present application was filed in the United States on May 22, 1987. Applicants have submitted declarations from the inventors and various U.S. researchers to establish an earlier conception and reduction to practice data. It is not fully clear what exact date ~~the~~ Applicants are entitled to. It would appear to be no earlier than the date at which a sample and enabling disclosure (Z. Phys. B- Condensed matter article) was brought to the United States from switzerland by Praveen Chaudhari on approximately October 17, 1986 (see Chaudhari Declaration). It would also appear to be no later than the date at which the samples were tested <sup>in U.S.</sup> to show superconductivity on approximately December 13, 1986 (see Green Declaration, page 1 of Exhibit D). In view of the fact that there is no art of record that discloses <sup>Ba</sup>La-~~Pr~~-Cu-O as a superconducting system prior to January 1, 1987, there is no need for us at this time to make a definite judgement as to which date represents reduction to practice. For the purpose of record a number of references having a filing date later than January 1, 1987 are cited here. Each clearly teaches

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superconductivity in a material containing lanthanum, alkaline earth, copper and oxygen but are not considered prior art by this Office. It should be noted that the Ganguly reference recites December 1986 at the top of the article. This was not the date of publication as shown by the 1987 references cited at the end of the article. An exact date has not been established, however, it is certain to be later than January 1, 1987.

20. The following is a quotation of the appropriate paragraphs of 35 U.S.C. § 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless --

(a) the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicant for a patent.

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

21. The following is a quotation of 35 U.S.C. § 103 which forms the basis for all obviousness rejections set forth in this Office action:

A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Subject matter developed by another person, which qualifies as prior art only under subsection (f) or (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same

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person or subject to an obligation of assignment to the same person.

The "person having ordinary skill" in this art has the capability of understanding the scientific and engineering principles applicable to the claimed invention. The references of record in this case reasonably reflect this level of skill.

22. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Shaplygin et al, Nguyen et al, Michel et al. (Mat. Res. Bull. and Revue de Chimie). Shalygin discloses  $\text{Ln}_{2-4}\text{M}_x\text{CuO}_4$  where M is Ca, Sr, Ba and Pb and Lu is La, Pr, Nd, Sm, Eu and Gd.  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_4$  is disclosed on page 823. Nguyen discloses  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ . Michel (Revue de chimie) discloses  $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_4$  where A=Ca, Sr, Ba. Michel (Mat. Res. Bull.) discloses  $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$  and  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+x}$ . Although these references fail to disclose superconductivity, each appears to fall within the scope of the presently claimed subject matter. Accordingly, the burden of proof is upon applicants to show that the instantly claimed subject matter is different from and unobvious over that taught by this reference. See In re Brown, 173 U.S.P.Q. 685, 688; In re Best, 195 U.S.P.Q. 430 and In re Marosi, 218 U.S.P.Q. 289, 293.

23. Claims 1-2, 5-11, 40-44, 46, 48, 49, 51-54, 60, 62, and 66 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of

Art Unit 115

Perron-Simon et al, Mossner et al, Chincholkar et al, Amad et al, Blasse et al, Kurihara et al and Anderton et al. Perron-Simon discloses  $\text{Ba}_2\text{La}(\text{Nb}_{13/3})\text{O}_{15}$ . Mossner discloses  $\text{Ba}_6\text{YNb}_{4.5}\text{O}_{18}$ . Chincholkar discloses  $\text{Ba}(\text{Ln}_{0.5}\text{B}_{0.5})\text{O}_3$ . Ahmad discloses  $\text{Ba}_2\text{YNbO}_6$ . (page 43). Blasse discloses  $\text{Ba}_2\text{GdNbO}_6$ . Kurihara discloses  $\text{Ba}(\text{YNb})_{0.5}\text{O}_3$ . Anderton discloses  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ . Although none of the cited references discuss superconductivity, each appears to fall within the scope of the claims. Furthermore, Ogashi (not considered prior art) teaches that La-Sr-Nb-O systems are superconducting. The case law cited at the end of the previous paragraph applies here as well.

24. Because of the fast moving pace of research in the field of high temperature superconductors, many scientific developments in this area are available as "preprints" many weeks or months prior to publication in a journal. It is the Examiner's position that such preprints are prior art as a printed publication under 35 U.S.C. 102(a) or (b) as of the date they are first distributed. ^See 3M v. Ansul, 213 U.S.P.Q. 1024, 1037. Any information of the above noted type that is material to the presently claimed subject matter available prior to the effective filing date of this application that applicant(s) are aware of should promptly be made of record pursuant to M.P.E.P. 609 and 37 CFR 1.56.

25. Any evidence to be presented in accordance with 37 CFR 1.131 or 1.132 should be submitted before final rejection in order to



Serial No. 053,307


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be considered timely. It is anticipated that the next Office  
Action <sup>may</sup> ~~will~~ be a final rejection.

26. Any inquiry concerning this communication or earlier communications from the examiner should be directed to John Boyd whose telephone number is (703) 557-8777.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 557-2517.

JBoyd   
August 07, 1990

PAUL LIEBERMAN  
SUPERVISORY PRIMARY EXAMINER  
ART UNIT 115

## LIST OF REFERENCES CITED BY APPLICANT

(Use several sheets if necessary)

ATTY. DOCKET NO.

Y0987-074

SERIAL NO.

06/053,307

APPLICANT

J. G. Bednorz et al

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5/22/87

GROUP

## U.S. PATENT DOCUMENTS

| *EXAMINER<br>INITIAL |    | DOCUMENT NUMBER | DATE | NAME | CLASS | SUBCLASS | FILING DATE<br>IF APPROPRIATE |
|----------------------|----|-----------------|------|------|-------|----------|-------------------------------|
|                      | AA |                 |      |      |       |          |                               |
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## FOREIGN PATENT DOCUMENTS

|  |    | DOCUMENT NUMBER | DATE | COUNTRY | CLASS | SUBCLASS | TRANSLATION |    |
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|  |    |                 |      |         |       |          | YES         | NO |
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## OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

|    |    |    |   |
|----|----|----|---|
| JG | AR | 14 | Thin Solid Films 54,(1978) 129-136 "Superconducting BaPb. Bi O Ceramic Films Prepared by R.F. Sputtering" by L.R. Gilbert et al                         |
|    |    |    |   |
| JG | AS | 15 | Proceedings of the 13th Conf. on Solid State Devices, Tokyo, 1981 pp.313-318 (Invited) New Materials for Josephson Junction Devices by T. Inamura et al |
|    |    |    |   |
| JG | AT | 16 | Europhysics letters, 3(3), pp 379-385 (1982) "Susceptibility Measurements Support High-T <sub>c</sub> Superconductivity..." by J.G. Bednorz et al       |
|    |    |    |   |

EXAMINER

DATE CONSIDERED

7/28/90

\*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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Y0987-079

SERIAL NO.

06/053,307

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J. G. Bednorz et al

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U.S. PATENT DOCUMENTS

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OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

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John B. ...

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7/17/90

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| JP | AR | 10 | Ibaraki Electrical Comm. Lab, "New Devices Using Superconducting $\text{BaPb}_{0.7}\text{Bi}_{0.3}\text{O}_3$ (BPB) Thin Films" by T. Murakami et al   |
| JP | AS | 11 | Jap. Journal of Appl. Phys. Vol. 21, No. 7, July 1982, pp L437-L439, "Temperature Dependence of Max. DC Johnson Current through Grain Boundary Junctions in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ Films" by M. Suzuki et al |
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EXAMINER

J. G. Bednorz

DATE CONSIDERED

7/17/92

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Y0987-074

SERIAL NO.

06/053,307

APPLICANT

J. G. Bednorz et al

FILING DATE

5/22/87

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OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

|           |    |                 |  |
|-----------|----|-----------------|--|
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|           | AS | 8               | Jap. Journal of Appl. Phys. Vol. 19, No. 5, May 1980 pp L231-L234, "Preparation of Superconducting BaPb <sub>1-x</sub> Bi <sub>x</sub> O Thin Films..." by M. Suzuki et al       |
| 1/2       | AT | 9               | J. Appl. Phys. 53(3), Mar 1982, pp. 1622-1630 "Preparation and Properties of Superconducting BaPb <sub>1-x</sub> Bi <sub>x</sub> O Thin Films by Sputtering" by M. Suzuki et al. |
|           |    |                 |  |
| EXAMINER  |    | DATE CONSIDERED |  |
| John Bzyl |    | 7/17/90         |  |

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Y0987-0-4

SERIAL NO.

06/053,307

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J. G. Bednorz et al

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|          | AT | 6               | Mat. Res. Bull. Vol. 8, pp. 777-784, 1973, "High Temperature Superconductivity in the Li-Ti-O Ternary System" by D. C. Johnson et al   |
| EXAMINER |    | DATE CONSIDERED |  |
| JH Ryl   |    | 7/17/77         |  |

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Y0987-074 106/053,307  
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J. G. Bednorz et al  
FILING DATE  
5/22/87 GROUP

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OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

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| Jh | AR | 1. Z. Phys. B - Condensed Matter 64, 189-193 (1986) "Possible High T <sub>c</sub> Superconductivity in the Ba-La-Cu-O System" by J. G. Bednorz et al   |
|    | AS | 2. Revue de Chimie minérale, t. 21, 1984, p. 407, "Oxygen Intercalation in Mixed Valence Copper Oxides Related to the Perovskites" by C. Michel et al  |
|    | AT | 3. Mat. Res. Bull., Vol. 20, pp. 667-671, 1985 Pergamon Press Ltd, "The Oxygen Defect Perovskite, Ba <sub>1-x</sub> La <sub>x</sub> Cu <sub>1-y</sub> O <sub>3-y</sub> , A Metallic Detector" by C. Michel et al |

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7/17/87

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INVENTOR'S DECLARATION  
FOR FILING: TRANSMITTAL LETTER RE: INVENTOR'S DECLARATION

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In re application of: J.G. BEDNORZ ET AL  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION...  
Serial No. 06/053,307; Docket No. Y0987-074 Att: JES  
Received in the U.S. Patent & Trademark Office:  
No. of pages of specification     : No. of pages of claims       
No. of sheets of drawings:       
Declaration is attached to specification.  
All fees are charged to our Account No. 09-0468

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FOR FILING: TRANSMITTAL LETTER RE: INVENTOR'S  
DECLARATION

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In re application of: J.G. BEDNORZ ET AL  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION  
Serial No. 06/053,307; Docket No. Y0987-074 Att: JES  
Received in the U.S. Patent & Trademark Office:  
No. of pages of specification     : No. of pages of claims       
No. of sheets of drawings:       
Declaration is attached to specification.  
All fees are charged to our Account No. 09-0468

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TO SEPARATE, HOLD TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

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|---|---|--|-----------|------------------------|-------------------|---|
| FORM PTO-892<br>(REV. 3-78)   |   | U.S. DEPARTMENT OF COMMERCE<br>PATENT AND TRADEMARK OFFICE |           | SERIAL NO.<br>83202    | GROUP/UNIT<br>115 | ATTACHMENT<br>TO<br>PAPER<br>NUMBER<br>20 |
| NOTICE OF REFERENCES CITED  |   |  |           | APPLICANT(S)<br>Bedone |                   |   |
|   |   |  |           |                        |                   |   |
| U.S. PATENT DOCUMENTS   |   |  |           |                        |                   |   |
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| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |   |  |           |                        |                   |   |
| R   | Rao "High Tc Superconductivity in Quasi Two Dimensional<br>Compound Semiconductors" v 56 Jan 1987 p 47-49       |  |           |                        |                   |   |
| S   | Ganguly "High Tc Superconductivity in oxides" v 10, S. S. Rao<br>Proc. Int. Acad. Sci. v 97(3) Feb 1987 p 14(2) |  |           |                        |                   |   |
| T   | U.S. Pat. App. No. 7,100,000 v 10(1) Jan 1987 p 21-23   |  |           |                        |                   |   |
| U   | Cava "Bulk Superconductivity" v 36 K. L. ...<br>Phys. Rev. Lett. v 58(4) Jan 1987 p 311-312                     |  |           |                        |                   |   |
| EXAMINER<br>John Byrd   |   | DATE<br>7/1/90   |           |                        |                   |   |
| * A copy of this reference is not being furnished with this office action.<br>(See Manual of Patent Examining Procedure, section 707.05 (a).) |   |  |           |                        |                   |   |

TO SEPARATE, HOLD TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

| FORM PTO-892<br>(REV. 3-78)   |   | U.S. DEPARTMENT OF COMMERCE<br>PATENT AND TRADEMARK OFFICE |         | SERIAL NO.<br><b>53367</b>      | GROUP/PART UNIT<br><b>115</b> | ATTACHMENT TO PAPER NUMBER<br><b>70</b> |                      |           |
|---|---|--|---------|---------------------------------|-------------------------------|---|----------------------|-----------|
| <b>NOTICE OF REFERENCES CITED</b>                                       |   |  |         | APPLICANT(S)<br><b>Bellcore</b> |                               |   |                      |           |
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| #   | DOCUMENT NO.  | DATE   | NAME    | CLASS                           | SUB-CLASS                     | FILING DATE IF APPROPRIATE              |                      |           |
| A   |   |  |         |                                 |                               |   |                      |           |
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| FOREIGN PATENT DOCUMENTS  |   |  |         |                                 |                               |   |                      |           |
| #   | DOCUMENT NO.  | DATE   | COUNTRY | NAME                            | CLASS                         | SUB-CLASS                               | PERTINENT SHTS. DWG. | PP. SPEC. |
| L   |   |  |         |                                 |                               |   |                      |           |
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| P   |   |  |         |                                 |                               |   |                      |           |
| Q   |   |  |         |                                 |                               |   |                      |           |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.) |   |  |         |                                 |                               |   |                      |           |
| R   | Nguyen "Oxygen Delet K <sub>2</sub> MoF <sub>6</sub> type oxides..."<br>Int'l J. Solid State Chem. v. 39 1991 p. 111-122  |  |         |                                 |                               |   |                      |           |
| S   | Shetty "Preparation of Rn-Polymer at H..."<br>Russian J. Inorg. Chem. v. 21(6) 1979 p. 870-41   |  |         |                                 |                               |   |                      |           |
| T   | Bull. Phase Diagrams of Al <sub>2</sub> (LaAlO <sub>3</sub> ) <sub>2</sub> (Si <sub>2</sub> Li <sub>2</sub> ) <sub>2</sub> ...<br>Mat. Res. Bull. v. 18 1983 p. 111-122 |  |         |                                 |                               |   |                      |           |
| U   | Chen "Chemical synthesis..."<br>C.R. Acad. Sci. Paris (283) 1976 p. 37-38   |  |         |                                 |                               |   |                      |           |
| EXAMINER  |   | DATE   |         |                                 |                               |   |                      |           |
| <i>[Signature]</i>  |   | 7/1/90   |         |                                 |                               |   |                      |           |

\* A copy of this reference is not being furnished with this office action.  
(See Manual of Patent Examining Procedure, section 707.05 (a).)

| FORM PTO-892<br>(REV. 3-78)   |  | U.S. DEPARTMENT OF COMMERCE<br>PATENT AND TRADEMARK OFFICE         |  | SERIAL NO.<br><div style="font-size: 1.5em; font-family: cursive;">53307</div>       | GROUP/ART UNIT<br><div style="font-size: 1.5em; font-family: cursive;">111</div> | ATTACHMENT TO PAPER NUMBER |      |         |       |           |                            |                      |           |
|---|--|--|--|--|--|----------------------------|------|---------|-------|-----------|----------------------------|----------------------|-----------|
| <b>NOTICE OF REFERENCES CITED</b>   |  |  |  | APPLICANT(S)<br><div style="font-size: 1.5em; font-family: cursive;">B. L. ...</div> |  |                            |      |         |       |           |                            |                      |           |
| U.S. PATENT DOCUMENTS   |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| *   | DOCUMENT NO.   |  |  |  |  |                            | DATE | NAME    | CLASS | SUB-CLASS | FILING DATE IF APPROPRIATE |                      |           |
| A   |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
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| FOREIGN PATENT DOCUMENTS  |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| *   | DOCUMENT NO.   |  |  |  |  |                            | DATE | COUNTRY | NAME  | CLASS     | SUB-CLASS                  | PERTINENT SHTS. DWG. | PP. SPEC. |
| L   |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
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| Q   |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| R   | Messrs. Bag B <sub>05</sub> , Mb <sub>4</sub> , O <sub>18</sub> (B. S. & E.) " |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| S   | See also U.S. Comm. Pat. 1,111,111 v. 1111 p. 1111-11                          |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| T   | Chickadee Thermal behavior of composition of matter                            |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| U   | Thermal A.L.C., (IL) L.I.E. 1910 p. 1111                                       |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| V   | Almond "Effect of environmental factors on growth"                             |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| W   | Sp. 1,111,111 v. 1111 1910 p. 34-35  |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| X   | Blau, "Electronics and a method of Spectra / Control Room"                     |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| Y   | Sol. J. Sol. Selection v. 6 1913 p. 313, 118                                   |  |  |  |  |                            |      |         |       |           |                            |                      |           |
| EXAMINER  |  | DATE   |  |  |  |                            |      |         |       |           |                            |                      |           |
| <div style="font-size: 1.5em; font-family: cursive;">John B. 20</div>   |  | <div style="font-size: 1.5em; font-family: cursive;">7/11/40</div> |  |  |  |                            |      |         |       |           |                            |                      |           |
| * A copy of this reference is not being furnished with this office action.<br>(See Manual of Patent Examining Procedure, section 707.05 (a).) |  |  |  |  |  |                            |      |         |       |           |                            |                      |           |

TO SEPARATE, HOLD TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

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| FORM PTO-892<br>(REV. 3-78)   |  | U.S. DEPARTMENT OF COMMERCE<br>PATENT AND TRADEMARK OFFICE |         | SERIAL NO.<br><div style="font-size: 1.2em;">83307</div>     | GROUP/ART UNIT<br><div style="font-size: 1.2em;">111</div> | ATTACHMENT<br>TO<br>PAPER<br>NUMBER |   |
| NOTICE OF REFERENCES CITED  |  |  |         | APPLICANT(S)<br><div style="font-size: 1.2em;">Bedoune</div> |  |                                     |   |
|   |  |  |         |  |  |                                     |   |
| U.S. PATENT DOCUMENTS   |  |  |         |  |  |                                     |   |
| *   | DOCUMENT NO.   | DATE   | NAME    | CLASS  | SUB-CLASS  | FILING DATE IF APPROPRIATE          |   |
| A   |  |  |         |  |  |                                     |   |
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| FOREIGN PATENT DOCUMENTS  |  |  |         |  |  |                                     |   |
| *   | DOCUMENT NO.   | DATE   | COUNTRY | NAME   | CLASS  | SUB-CLASS                           | PERTINENT<br>SHTS.<br>DWG. PP.<br>SPEC. |
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| M   |  |  |         |  |  |                                     |   |
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| P   |  |  |         |  |  |                                     |   |
| Q   |  |  |         |  |  |                                     |   |
| OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)   |  |  |         |  |  |                                     |   |
| R   | Anionic Production of conducting oxide powder          |  |         |  |  |                                     |   |
| S   | Powder Mat. No. 1 1979 p. 11-21                        |  |         |  |  |                                     |   |
| T   | Organic Production of Superconductivity in 11 1/2 7... |  |         |  |  |                                     |   |
| U   | J. L. Temp. Phys. & (4 1/2, 6) 1987 p. 11-7            |  |         |  |  |                                     |   |
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| EXAMINER  |  | DATE   |         |  |  |                                     |   |
| <div style="font-size: 1.2em;">JL</div>   |  | <div style="font-size: 1.2em;">7/11/90</div>               |         |  |  |                                     |   |
| * A copy of this reference is not being furnished with this office action.<br>(See Manual of Patent Examining Procedure, section 707.05 (a).) |  |  |         |  |  |                                     |   |

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J.G. BEDNORZ ET AL.  
Serial No: 06/053,307 Group No.: 115  
Filed: 05/22/87 Examiner: Dennis Albrecht  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION  
Commissioner of Patents and Trademarks  
Washington, D.C. 20231

EXPRESS MAIL CERTIFICATE

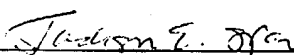
"Express Mail" label number B33592766  
Date of Deposit June 22, 1988

I hereby certify that the following *attached* paper or fee

Transmittal Letter Re: Inventor's Declaration with Respect to  
High T<sub>c</sub> Superconductivity  
Declaration  
Return Postcard

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Jackson E. Stanland  
(Typed or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

NOTE: Each paper must have its own certificate and the "Express Mail" label number as a part thereof or attached thereto. When, as here, the certification is presented on a separate sheet, that sheet must (1) be signed and (2) fully identify and be securely attached to the paper or fee it accompanies. Identification should include the serial number and filing date of the application as well as the type of paper being filed, e.g. complete application, specification and drawings, responses to rejection or refusal, notice of appeal, etc. If the serial number of the application is not known, the identification should include at least the name of the inventor(s) and the title of the invention.

NOTE: The label number need not be placed on each page. It should, however, be placed on the first page of each separate document, such as, a new application, amendment, assignment, and transmittal letter for a fee, along with the certificate of mailing by "Express Mail." Although the label number may be on checks, such a practice is not required. In order not to deface formal drawings it is suggested that the label number be placed on the back of each formal drawing or the drawings be accompanied by a set of informal drawings on which the label number is placed.

DOCKET NO. Y0987-074

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: June 22, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

TRANSMITTAL LETTER RE: INVENTOR'S DECLARATION  
WITH RESPECT TO HIGH T<sub>c</sub> SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Enclosed is an executed declaration of the inventors in further support of their activities in the United States in 1986. Submission of this declaration completes the material to be forwarded to the U.S. Patent and Trademark Office. Although only Dr. Mueller's signature was omitted from the earlier filed inventors' declaration, both inventors have signed the enclosed declaration.

Respectfully submitted,

By Jackson E. Stanland  
Jackson E. Stanland - Attorney  
Registration No. 24,444  
(914) 241-4059

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598

YO987-074

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 21, 1988

Filed: 05/22/87 : Serial No.: 06/053,307

Group Art Unit: 115 : Examiner: Dennis Albrecht

FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF J. GEORG BEDNORZ AND K.A. MUELLER  
WITH RESPECT TO HIGH T<sub>c</sub> SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

We, J. Georg Bednorz and K.A. Mueller, hereinafter say and declare the following:

1. We are the inventors of the contribution described and claimed in the subject U.S. patent application. This application describes our earlier discovery of high temperature superconductivity in ceramic copper oxide materials. In particular, one of the earlier systems in which we worked was comprised of Ba-La-Cu-oxides which exhibited superconducting onset temperatures in the mid *w* *Lr*  
*over* thirty K range.

2. We conducted extensive research on these materials to establish their superconductivity in our laboratory in Zurich, Switzerland. This work traced back to early 1986 and was described in a publication by us that appeared in Z. Phys. B - Condensed Matter 64, 189-193 (1986). This article describes, among other items, resistivity versus temperature measurements that we made on samples of this material to show its superconductive behavior. We subsequently submitted for publication and had published additional articles describing these high T<sub>c</sub> oxide superconductors.

3. On approximately October 16, 1986, we gave Praveen Chaudhari (Vice-President, Science at the Yorktown Research Laboratory of IBM Corporation) six samples of the high temperature superconductive ceramic oxide material that we had described in our aforementioned Z. Physik B. publication. Praveen Chaudhari brought these samples back to the U.S. when he returned after

visiting with us on or about October 16, 1986. These samples were given to him so that experimentation and measurement could be performed on the samples in the United States. We knew the individuals (Richard Greene and Chang C. Tsuei) who would be involved in the measurements in the United States and discussed the measurements with these individuals in approximately the third week of October, 1986. We maintained telephone and computer communications with these individuals from that time continually through the remainder of 1986 and into 1987.

4. It was decided by us that Richard Greene would do specific heat measurements on these samples while magnetic measurements would be done by us in our Zurich laboratory. Greene worked for Chang Tsuei and discussed with him the nature of the experiments and development activities to be performed at the aforementioned Yorktown lab. We provided guidance to Richard Greene and Chang Tsuei by describing the nature of these superconducting samples and the types of properties that we had measured relative to these samples. One of us (K.A. Mueller) also discussed confirmation of our resistivity versus temperature measurements with said Chang Tsuei in a telephone conversation in October, 1986.

5. The early work conducted by the individuals in the Yorktown laboratory on our superconducting samples occurred with the supervision and guidance that we furnished to these Yorktown scientists. Additionally, we provided a preprint to Richard Greene of an article that we subsequently published in Europhysics Letters 3, (3), pp. 379-385 (1987). This article was given to Greene in October, 1986 and described magnetic measurements on these superconducting samples.

6. We were aware of the work being conducted on our samples at the Yorktown lab and were in contact with the individuals there, and particularly Richard Greene, who reported to Chang Tsuei. Since the specific heat measurements generally take longer, we had considerable interactions with Rick Green over a period of time from about October 22, 1986 through December, 1986, concerning his specific heat measurements. We also were made aware of Chang Tsuei's measurements of resistivity versus temperature of the Ba-La-Cu-oxide samples, which confirmed our earlier resistivity versus temperature measurements.

7. We further declare that all statements made hereinabove based on our own knowledge are true and that all statements made on information and belief are believed to be true. We further declare



that these statements are made with the knowledge that willful false state- ments and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of our Patent Application or any patent issuing thereon.

J. Georg Bednorz  
J. GEORG BEDNORZ

DATE: May 30. 1988

K. Alex Müller

K.A. MUELLER

DATE: May 27. 1988

FOR FILING: SUBMISSION OF DECLARATION OF J. GEORG BEDNORZ  
EXPRESS MAILING: #B29953175 Date of Deposit: 5/25/88

PLEASE STAMP & RETURN TO US

In re application of: J.G. Bednorz et al.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMP.

Serial No.: 06/053,307 Docket No.: YO987-074 Atty.: JES

Received in the U.S. Patent & Trademark Office

No. of pages of specification: No. of pages of claims

No. of sheets of drawings:

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

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FOR FILING: SUBMISSION OF DECLARATION OF  
J. GEORG BEDNORZ  
EXPRESS MAILING: #B29953175 Date of Deposit: 5/25/88

PLEASE STAMP & RETURN TO US

In re application of: J.G. BEDNORZ ET AL.

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMP.

Serial No. 06/053,307; Docket No.: YO987-074 Atty.: JES

Received in the U.S. Patent & Trademark Office:

No. of pages of specification: No. of pages of claims

No. of sheets of drawings:

Declaration is attached to specification.

All fees are charged to our Account No. 09-0468

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: May 25, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

SUBMISSION OF DECLARATION OF J. GEORG BEDNORZ

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Enclosed is an executed declaration of J. Georg Bednorz, relative to his activities toward a completion of his invention in the United States. Dr. K.A. Mueller, his co-inventor, is unavailable for execution of the declaration until June, 1988.

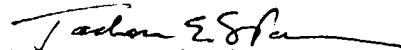
A previously prepared declaration, identical to the enclosed declaration, was sent Air Express from Zurich on about March 30, 1988, but was lost and never arrived at the office of the undersigned. That declaration was executed by both Drs. Bednorz and Mueller.

As soon as Dr. Mueller is available, he will be contacted and his executed declaration will be sent to the Patent and Trademark Office.

The enclosed declaration sets forth the cooperation and guidance given by Drs. Bednorz and Mueller to individuals in the United States, in order to enable those U.S. workers to duplicate the previous accomplishments of the inventors in Zurich, Switzerland.

Respectfully submitted,

By



Jackson E. Stanland - Attorney  
Registration No. 24,444  
(914) 241-4059

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 21, 1988

Filed: 05/22/87 : Serial No.: 06/053,307

Group Art Unit: 115 : Examiner: Dennis Albrecht

FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF J. GEORG BEDNORZ AND K.A. MUELLER  
WITH RESPECT TO HIGH  $T_c$  SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

We, J. Georg Bednorz and K.A. Mueller, hereinafter say and declare the following:

1. We are the inventors of the contribution described and claimed in the subject U.S. patent application. This application describes our earlier discovery of high temperature superconductivity in ceramic copper oxide materials. In particular, one of the earlier systems in which we worked was comprised of Ba-La-Cu-oxides which exhibited superconducting onset temperatures in the mid to upper thirty K range.

2. We conducted extensive research on these materials to establish their superconductivity in our laboratory in Zurich, Switzerland. This work traced back to early 1986 and was described in a publication by us that appeared in Z. Phys. B - Condensed Matter 64, 189-193 (1986). This article describes, among other items, resistivity versus temperature measurements that we made on samples of this material to show its superconductive behavior. We subsequently submitted for publication and had published additional articles describing these high  $T_c$  oxide superconductors.

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7. We further declare that all statements made hereinabove based on our own knowledge are true and that all statements made on information and belief are believed to be true. We further declare

that these statements are made with the knowledge that willful false state- ments and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of our Patent Application or any patent issuing thereon.

J. Georg Bednorz  
J. GEORG BEDNORZ

DATE:

11. 5. 88

\_\_\_\_\_  
K.A. MUELLER

DATE:

FOR FILING: SUBMISSION OF DECLARATIONS (ORR & CHAUDHARI)

FOR FILING: SUBMISSION OF DECLARATIONS (ORR & CHAUDHARI)

PLEASE STAMP & RETURN TO US

In re application of: J.G. BEDNORZ ET AL.  
NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
For: TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION  
Serial No. 05/053,307; Parker No. YO987-074      Atty. JES

Received in the U.S. Patent & Trademark Office: \_\_\_\_\_

No. of pages of specification: \_\_\_\_\_ No. of pages of claims: \_\_\_\_\_

No. of figures: \_\_\_\_\_

See Remarks for more details re specification. 28

All fees are charged to our Account No. 09-0462

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J.G. BEDNORZ ET AL

Serial No: 06/053,307

Group No: 115

Filed: 05/22/87

Examiner: Dennis Albrecht

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks

Washington, D.C. 20231

CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)

I hereby certify that the *attached* correspondence comprising:

Transmittal Letter

Two (2) Declarations in support of invention in the United States

*OK  
C. J. Stanland*

is being deposited with the United States Postal Service as first class mail in an envelope addressed to:

*Commissioner of Patents and Trademarks*

*Washington, D.C. 20231*

on April 22, 1988

Jackson E. Stanland

(Type or print name of person mailing paper)

*Jackson E. Stanland*

(Signature of person mailing paper)

DOCKET NO. YO987-074



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: April 22, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

SUBMISSION OF DECLARATIONS

RE: ACTS OF INVENTION IN THE UNITED STATES

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

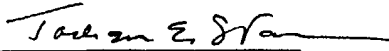
Sir:

Enclosed are declarations of Bradford G. Orr and Praveen Chaudhari relative to activities in high  $T_c$  superconductivity. These declarations were mentioned in applicants' transmittal letter dated March 31, 1988. Because Drs. Orr and Chaudhari were not available as quickly as it was believed they would be, their declarations were delayed relative to the expected times of delivery noted in applicants' 3-31-88 letter.

The declarations of Bednorz and Mueller have not been received yet, but I have been informed that they were executed and mailed to the United States. These remaining declarations will be filed in the Patent and Trademark Office upon receipt.

Respectfully submitted,

By



Jackson E. Stanland - Attorney  
Registration No. 24,444  
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IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598

Y0987-074

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS: J. G. Bednorz et al

DATE: April 18. 1988

SERIAL NO.: 06/053,307

ART UNIT: 111

FILING DATE: 05/22/87

EXAMINER:

FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF PRAVEEN CHAUDHARI RELATIVE TO HIGH  $T_C$   
SUPERCONDUCTIVITY

TO: The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

I, Praveen Chaudhari, hereby declare and say that:

1. During 1986 I was Vice President, Science, for the Research Division of International Business Machines Corporation, the assignee of the subject patent application. In my capacity as vice president, I had operational responsibility for all of the activities relating to science in the Research Division's main laboratory at Yorktown Heights, New York, and additionally had responsibility and control concerning the strategy, growth, and

resources in the general area of science in the IBM Research laboratories located in Zurich, Switzerland and Almaden, California. It was my general responsibility to determine the research projects to be conducted at these various laboratories and to routinely check with the personnel at these laboratories to determine that the strategy was being followed. Additionally, through my own communications and examination of regular progress reports concerning activities in science in the three research laboratories, each laboratory was aware of the activities in science at each other laboratory, and in many instances collaboration between scientists at 2 or 3 of the laboratories could and did occur. In many instances, the science activities at the different laboratories complement the activities at the other laboratories in order to provide a cohesive and directed research effort.

2. The work of Alex Mueller and J. Georg Bednorz at IBM's Zurich Research laboratory which lead to their discovery of high temperature superconductivity as revealed in their paper in Z. Phys. B-Condensed Matter 64, 189-193 (1986) was known to me, dating back to 1982. I spoke with Alex Mueller at that time about techniques which may be

used to increase the electron concentration in oxide materials in order to obtain higher critical transition temperatures in such materials. One technique which we discussed for accomplishing this was the application of an electric field to essentially create an inversion layer having an increased electron density. At that time, he and I believed that the provision of higher critical transition temperatures in these materials would require higher electron density and the application of an electric field was one of the techniques we discussed for achieving this. In the time period between our 1982 conversation and 1986, I followed the work of Alex Mueller and J. Georg Bednorz and, having responsibility in my role as vice president, science, I was aware of their work through the issuance of monthly progress (activity) reports from the Zurich Research laboratory. I also visited the Zurich laboratory on a regular basis to confer with scientific personnel at the laboratory in order to review their programs and the progress in these programs.

3. In July, 1986, I visited the Zurich laboratory of Alex Mueller and J. Georg Bednorz and talked with Alex Mueller concerning his experiments on what are now known as high

$T_c$  oxide superconductors. More specifically, I was shown the data of Mueller and Bednorz relative to the superconducting La-Ba-Cu-O oxide superconductors that they had discovered and measured.

4. While I was visiting with Mueller and Bednorz in July, 1986, they gave me a copy of the aforementioned technical paper that they had submitted to Z. Phys. B. At that time, Alex Mueller asked me to withhold dissemination of the paper until the end of August or beginning of September 1986. This I did.
5. I returned to the United States from the Zurich laboratory shortly thereafter, and held my copy of the submitted Mueller and Bednorz paper until the date indicated by them for dissemination to other scientists at IBM's research laboratory in Yorktown Heights New York. At that time, I gave a copy of this paper to Alex Malozemoff, a senior manager in the Physical Sciences Department at the Yorktown Laboratory. Alex Malozemoff, who reported to me, said that he gave a copy of the paper to Chang Tsuei and Richard L. Greene, both of whom reported to Alex Malozemoff and are scientists at the Yorktown Research Laboratory.

6. In Mid October, 1986, I made a return trip to the IBM Zurich Research Laboratory and again met with Alex Mueller, who told me that magnetic measurements had been completed on the superconducting materials that he described and showed me in July 1986. Alex Mueller told me that his magnetic measurements convinced him of the superconductivity present in these materials. Our meeting occurred in the time frame October 15-17, 1986. While in Zurich, I discussed possible experiments that Mueller and Bednorz would do concerning these newly discovered superconductors and suggested an experiment in which persistent currents could be established in these new materials, the persistent currents then being measured using a SQUID device. Later, I received a computer message from Mueller and Bednorz relative to this experiment, indicating that it seemed to work as we had proposed.

7. Bednorz and Mueller told me that the magnetic measurements they made indicated to them the diamagnetic response of these superconducting materials. These measurements made even more convincing to them and to me their earlier contention that they had discovered a new class of superconducting materials having critical tran-

sition temperatures higher than any of those previously reported.

8. While I was at the Zurich Research Laboratory in October 1986, Alex Mueller gave me samples of the superconducting material discovered by himself and J. Georg Bednorz to bring to the United States for evaluation in the United States. These materials were samples of La-Ba-Cu-O oxides as described in the aforementioned Bednorz and Mueller technical paper appearing in Z. Phys. B. I returned to the United States on approximately October 17, 1986, bringing with me samples of Bednorz and Mueller's superconducting materials, and their resistivity and diamagnetic measurement data which proved high temperature superconductivity.

9. Prior to October 17, 1986, and in the general time period between about September 1, 1986 to October 17, 1986, I was aware (based on conversations with them) that Richard Greene and Chang Tsuei were in contact with Alex Mueller and J. Georg Bednorz in order to discuss work that could be done in the United States by Greene and Tsuei, using the Mueller and Bednorz samples. These samples had been requested from Mueller and Bednorz by Richard Greene and

Chang Tsuei, and I carried the samples from Zurich to the United States at their request.

10. Upon my return to the United States, I gave these samples to Richard Greene, who proceeded to do specific heat and resistivity measurements on these samples, under the general guidance of Mueller and Bednorz in Zurich, Switzerland. I met Chang Tsuei within approximately two weeks after I had given Greene the samples in order to ask him how the data and measurements were progressing. Chang Tsuei replied that he had done resistivity versus temperature measurements on the samples, and that the resistivity data was good, indicating a drop to zero resistivity at an onset temperature above 30°K. The specific heat data of Richard Greene was a bit inconclusive as I recall, but the resistivity data was excellent in indicating a resistivity drop substantially identical to that reported in the Mueller and Bednorz publication appearing in Z. Phys. B.

11. In October, 1986, I also asked Alex Mueller about his work with Bednorz dealing with the replacement of Ba by Ca and Sr. Alex Mueller informed me that experiments were in progress using these elements and that Sr substitution



gave promising results and that Ca substitution was also being done. These compositions were La-Sr-Cu-O oxides and La-Ca-Cu-O oxides.

12. In November and December 1986, I had further discussions with Alex Malozemoff, Richard Greene and Chang Tsuei regarding their work on these high  $T_c$  superconducting samples. I also contacted the Zurich Research laboratory in order to propose a press release on the Zurich discovery, which was recognized to be a significant achievement in science.

13. I know of no other facts which would present a factual situation different than that described hereinabove, and assert that the facts described hereinabove are based on my own experience and recollection concerning the events occurring relative to the discovery of high  $T_c$  superconductivity and the activities in the United States which were directed by me to re-establish the results first accomplished by Mueller and Bednorz in Zurich, Switzerland. With the exception of the acts conducted in Zurich by Mueller and Bednorz and my acts while visiting IBM's Zurich Laboratory, all acts described hereinabove occurred in the United States.

14. I, further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Praveen Chaudhari April 21, 1988

PRAVEEN CHAUDHARI

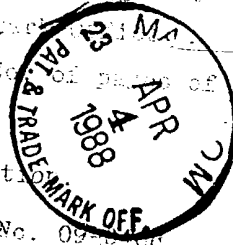
DATE

FOR FILING: SUBMISSION OF DECLARATIONS

PLEASE STAMP & RETURN TO US

In re application of: J.G. BEDNORZ ET AL  
NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
For: TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION  
Serial No. 06/053,307, Doc. No. Y0987-074 Atty.: JES

Received in the U.S. Patent & Trademark Office  
No. of pages of specification 1 No. of pages of claims 1  
No. of sheets of drawings 1



Information is attached to classification  
Fees are charged to our Account No. 09-1000

*Declarations*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: J.G. BEDNORZ ET AL.

Serial No: 06/053,307

Group No: 115

Filed: 05/22/87

Examiner: Dennis Albrecht

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

Commissioner of Patents and Trademarks

Washington, D.C. 20231

CERTIFICATE OF MAILING UNDER 37 CFR 1.8(a)

I hereby certify that the *attached* correspondence comprising:

Transmittal Letter

Seven (7) Declarations in support of invention in the United States

is being deposited with the United States Postal Service as first class mail in an envelope  
addressed to:

*Commissioner of Patents and Trademarks*

*Washington, D.C. 20231*

on March 31, 1988

Jackson E. Stanland

(Type or print name of person mailing paper)

*Jackson E. Stanland*

(Signature of person mailing paper)

DOCKET NO. Y0987-074

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 31, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

SUBMISSION OF DECLARATIONS

RE: ACTS OF INVENTION IN THE UNITED STATES

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Declarations in support of invention in the United States are  
offered by the following:

J. Georg Bednorz, inventor  
Carl A. Mueller, inventor  
Richard L. Greene  
Albert M. Torressen  
Chang C. Tsuei  
Sung Il Park  
Praveen Chaudhari  
Alexis P. Malozemoff  
Paul M. Horn  
Cheng-Chung John Chi  
Bradford G. Orr

YO987-074

These declarations describe acts of inventorship in the United States by and on behalf of the inventors Bednorz and Mueller, establishing the attainment of superconductivity in samples of Ba-La-Cu-O at onset temperatures greater than 23°K. These acts duplicate and extend the work first described by Bednorz and Mueller in Z. Phys. B-Condensed Matter, Vol. 64, p. 189, September, 1986. This technical article, as well as an IBM internal activity report describing the work of Bednorz and Mueller, were introduced into the United States in September, 1986 and established conception in the United States. The work of Greene and Tsuei, on behalf of and under the guidance and cooperation of Bednorz and Mueller, establishes reductions to practice in the United States of a superconductor having a transition temperature greater than 23°K. This work was witnessed and corroborated by the other people whose declarations are included.

A declaration by Dr. Bradford Orr had not been executed and returned in time to include it with the other declarations. It will be forwarded as soon as it is received (estimated delay - less than one week). The same is true for the declarations of the inventors Bednorz and Mueller. Their declaration, although having been executed by one of them (Bednorz) had not been executed by the other in time to include herewith. It will be forwarded to the Patent and Trademark Office as soon as it is received (which should be in about one week). The declaration of Praveen Chaudhari will be executed April 1, 1988 and then forwarded to the Patent and Trademark Office.

The declarations, generally describe three types of measurements performed prior to about December 8, 1986, on samples provided by Bednorz and Mueller, which are the following:

- (1) Resistivity versus temperature (Chang C. Tsuei)
- (2) Resistivity versus temperature in a magnetic field (Richard L. Greene)
- (3) Specific Heat (Richard L. Greene)

Measurement 1

Resistivity versus temperature was done by Chang C. Tsuei. This confirmed the data presented by Bednorz and Mueller in their Z. Phys. B. article. Witnesses corroborating Tsuei's measurements include Sung Il

Park, Albert M. Torressen, Paul M. Horn, Bradford G. Orr, Praveen Chaudhari, A.P. Malozemoff.

Measurement 2

Resistivity versus temperature in a magnetic field was done by Richard L. Greene. This further confirmed the data of Bednorz and Mueller and clearly established the superconducting nature of the samples provided by Bednorz and Mueller. Witnesses to this work include Albert M. Torressen and Thomas Penny.

Measurement 3

Specific heat measurements were done by Richard L. Greene and Albert M. Torressen and supplemented Greene's resistivity versus temperature measurements. Witnesses include Albert M. Torressen, Chang C. Tsuei, S. Von Molnar, M. W. Shafer, Sung Il Park, Thomas Penny, and Arthur R. Williams.

Relevant Law

35 U.S.C. 104

Acts of Conception: Mortsell v. Laurila, 301 F.2d 947, 133 USPQ 380 (1962)

In re Tansel 253 F.2d 241, 117 USPQ 188 (1958)

Clevenger v. Kooi, 190 USPQ 188 (1974)

Acts of Reduction to Practice: DeKando v. Armstrong 37 App. D.C. 314

Claims

All of the claims in this application are directed to the broad concepts first discovered and announced by Bednorz and Mueller. This discovery is attributed to these inventors by the rest of the world-wide

YO987-074

technical community, and only these inventors are entitled to broad claims to their discovery of high  $T_c$  copper oxide superconductors.

It is respectfully urged that the enclosed declarations and the ones to be filed very soon establish conception, diligence, and reduction to practice of the invention by the inventors in the United States at an early date prior to any reference known to applicants.

Respectfully submitted,

By Jackson E. Stanland  
Jackson E. Stanland - Attorney  
Registration No. 24,444  
(914) 241-4059

IBM Corporation  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, N.Y. 10598

Y0987-074



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 29, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF RICHARD L. GREENE  
WITH RESPECT TO HIGH  $T_c$  SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Richard L. Greene, hereby declare and say that:

1. I received a Ph.D in physics from Stanford University in 1967, and joined the San Jose, California laboratory of the Research Division of International Business Machines Corp. in 1970. I was the Manager of a group conducting research on organic superconductors and have worked in the field of superconductivity for 20 years. I transferred to IBM Corp. research laboratory in Yorktown, New York, in July 1986, and continued thereafter to conduct research on superconductive materials. From about October 1986 to the present I have worked on high  $T_c$  superconducting oxides.

2. At approximately the end of September - first week of October, 1986, my manager, Chang C. Tsuei, showed me a copy of an activity report from the Zurich Research Laboratory of IBM Corporation. This activity report described the work of J.G. Bednorz and K.A. Mueller and their discovery of new superconducting compositions. These materials were mixed copper oxide ceramics that exhibited an onset of superconductivity at a temperature significantly higher than the transition temperatures reported for previously known superconductors. Materials of this general class are now known in the art as high  $T_c$

YO987-074

superconductors. A true copy of this activity report is attached hereto and labeled Exhibit A.

3. Soon after reading this activity report and discussing it with Chang C. Tsuei, I called K.A. Mueller in Zurich and requested samples from him so that I could make measurements on these samples in the United States. This telephone call occurred approximately October 1 - October 6, 1986. My intent was to begin a research project on these materials, as I was very interested in them based on my previous work in superconductivity. My plan at that time was to do experiments which would be complementary to those being conducted by Bednorz and Mueller in Zurich, so that a maximum amount of information could be obtained about these new superconducting materials. Based on the data in this activity report and on the results of susceptibility measurements described to me by Alex Mueller in the aforementioned telephone call, I believed that a new class of superconducting materials with  $T_c$  greater than 30K had been discovered.

4. In approximately mid-October, 1986, Praveen Chaudhari, Vice-President, Science, at IBM's Watson Research Laboratory visited the Zurich IBM Lab. Based on my request for samples of the new superconducting material, Chaudhari told me that he had obtained them from Bednorz and Mueller and brought them back to the United States with him. These were about six samples in the Ba-La-Cu-O system. Chaudhari returned to the United States on or about October 20, 1986 and delivered these samples to me. Of these approximately six samples, they varied in the different amounts of La and Ba that were present. Only two of the samples were reported as being single phase materials.

5. Immediately upon receiving these samples, I was in contact with Bednorz and Mueller, via telephone and computer system links, in order to discuss with Bednorz and Mueller the experiments that I would conduct and also to obtain information from Bednorz and Mueller relative to the characteristics of the samples. I had planned to do specific heat measurements of the samples and also resistivity versus temperature measurements in the presence of a magnetic field. Because of the importance that I attributed to this work, I worked substantially full time on these superconductor materials in order to further characterize them. My first specific heat measurements occurred approximately October 29 and 30, 1986, while I measured resistivity versus temperature in the

YO987-074

presence of a magnetic field in late November, 1986. Continuously throughout the period, October 20, 1986 - February, 1987, I worked on a daily basis to further characterize these materials. At all times, I was in contact with Bednorz and Mueller, exchanged data with them, and worked in close cooperation with them. They provided information to me about the characteristics of the material, as well as providing me up-to-date information concerning the data they had obtained about these materials. A true copy of my computer log from October, 1986 - January 12, 1987 is attached hereto and labeled Exhibit B. Excerpts which do not relate to superconductivity have been deleted. In this exhibit, the identifier for K.A. Mueller is "KAM", while the identifier for J. G. Bednorz is "BED". Bednorz and Mueller are located in Zurich, Switzerland and the computer node for them is ZURLVM1. My identifier is "RGREENE". This computer log details my ongoing computer dialogue with Bednorz and Mueller relative to theirs and my activities on the high  $T_c$  superconductor materials. In addition to this computer correspondence, I also talked with Bednorz and Mueller via telephone.

6. During my specific heat measurements of these materials, as well as the measurements of resistivity versus temperature in the presence of a magnetic field, I was assisted by Albert M. Torressen, who was a laboratory specialist. I also discussed my laboratory experiments with Chang C. Tsuei, S. von Molnar, Merrill W. Shafer, Sung Il Park, Thomas Penney, and Arthur R. Williams.

7. The specific details of the apparatus and the data obtained in the specific heat measurements will be described in a separate statement by Albert M. Torressen, the laboratory specialist who worked with me to provide these measurements. Essentially, the specific heat of the apparatus was calculated to provide calibration and background specific heat, after which the sample was introduced into the apparatus and the total specific heat again measured. By subtracting the background specific heat, the specific heat of the superconducting sample is determined. This was done over a temperature range of approximately 2-50K.

8. The specific heat measurements of these superconducting samples were begun approximately October 21, 1986, and were conducted on a daily basis by me and Al Torressen through November and December, 1986.

These specific heat measurements and the curves which were plotted are representative of these superconducting materials, and are also representative of the specific heat versus temperature plots obtained on present samples of superconducting high  $T_c$  oxides.

9. In addition to the specific heat measurements described hereinabove and in the accompanying statement of Albert M. Torressen, I also performed measurements of resistivity versus temperature in the presence of a magnetic field, for the samples of Ba-La-Cu-O obtained from Bednorz and Mueller. The specific heat measurements were performed first on these samples, after which I measured resistivity versus temperature in an applied magnetic field, in order to further characterize these samples. These resistivity measurements were done at the end of November, 1986, and the beginning of December, 1986. Exhibit C is a true copy of nine pages of my data notebook, together with a copy of the cover of this notebook entitled "Zurich oxide BICO DATA (T,H)." The date "11/15/86" is also on the cover. Exhibit D is comprised of several pages of plots of resistivity versus temperature for these superconductor samples, as well as resistivity as a function of magnetic field at particular temperatures. In some instances, the  $RuO_2$  sample holder is taken into account into the plots. Generally, these plots represent the graphical expressions of the data contained in Exhibit C. Exhibit E is a composite plot incorporating the different plots found in Exhibit C, and shows resistivity versus temperature for different values of applied magnetic field. I used this composite plot at a seminar that I gave to other researchers at the Yorktown lab on December 12, 1986.

10. In order to obtain the data listed in Exhibit C, I used a laboratory belonging to Stephan von Molnar. Albert M. Torressen, who reported to von Molnar, showed me the necessary equipment to make these measurements, and I preceded to make them on my own. However, many people were aware of these resistivity measurements and viewed the data, including both Thomas Penney and Albert Torressen. In addition, Thomas Penney observed me making these measurements and understood the procedure and nature of my laboratory work.

11. I have numbered the data pages of Exhibit C in red in the upper right hand corner. Page 1 describes the sample set-up that I used for these measurements and the background data in order to ready the

apparatus for the resistivity versus temperature measurements. This sample was the BLCO -21 II, standing for Ba-La-Cu-Oxide material. Page 2 shows two views of the experimental apparatus and the calibration measurements made between particular terminals. The wires A, B, C and F are those which are also shown on page 1.

12. On pages 3, 4, and 5 I had listed the data that applied to the  $\text{RuO}_2$  sample holder and the four point probe. The sample was contacted with indium contacts and copper wires were attached to the indium contacts for the measurements. Both DC and AC measurements were made. The resistance of the sample is  $R_{FC}$  which was measured at various temperatures with the applied magnetic field  $H$  equal to zero (page 4). Pages 5 - 9 show further measurements that were made at different temperature settings and applied magnetic fields. All of the data on these pages were taken by me and entered by me in this notebook.

13. The plot of resistance versus temperature in exhibit D is a plot for the data which was obtained December 3 - December 5, 1986. Referring to Exhibit D, this plot shows the superconducting transition that begins to occur about 35K, where the transition shifts to the left in the presence of a magnetic field. This is an indication of a superconductor.

14. All acts performed by me as described hereinabove occurred in the United States.

15. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Richard L. Greene

RICHARD L. GREENE

DATE: 30 March 1988

IBM

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(Ext.) 8237  
Zurich Research Laboratory  
8803 Rüschlikon, Switzerland  
Telephone: 01 / 724 81 11  
Teleprinter: ITPS CODE ZRL

ACTIVITY REPORT  
MAY-JUNE, 1986

August 15, 1986

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MATERIAL SCIENCE T. Schneider, Mgr.

SURFACE & MATERIAL SCIENCES E. Courtens, Mgr., Project 4181

### Novel Research

#### Possible High- $T_c$ Superconductivity in the Ba-La-Cu-O System

J.G. Bednorz and K.A. Müller (Project 4196)

We observed a steep decrease of resistivity in sintered Ba-La-Cu-oxide samples, with the highest temperature of the onset in the 35 K range (Fig. 1).

The Ba-La-Cu-O system exhibits a number of oxygen deficient phases with perovskite-like layer-type structures. These are characterized by mixed-valent copper ions ( $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ ) and itinerant electronic states. In addition one expects polaron formation induced by the strong Jahn-Teller effect of  $\text{Cu}^{2+}$  in an octahedral oxygen environment. Thus our Ba-La-Cu-O system was anticipated to have considerable electron-phonon coupling and metallic conductivity.

Compounds with the composition  $\text{Ba}(x)\text{La}(5-x)\text{Cu}(5)\text{O}(5[3-y])$  have been prepared in polycrystalline form. Samples with  $x < 0.2$  and  $y > 0$ , annealed below  $900^\circ\text{C}$  under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound with  $\text{K}_2\text{NiF}_4$  type structure. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally a steep decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 35 K range. It is markedly reduced by high current densities (Fig. 1). The slow sensitivity decay towards low temperatures might possibly result from 2D superconducting fluctuations of perovskite layers of one of the phases present.

IBM CONFIDENTIAL

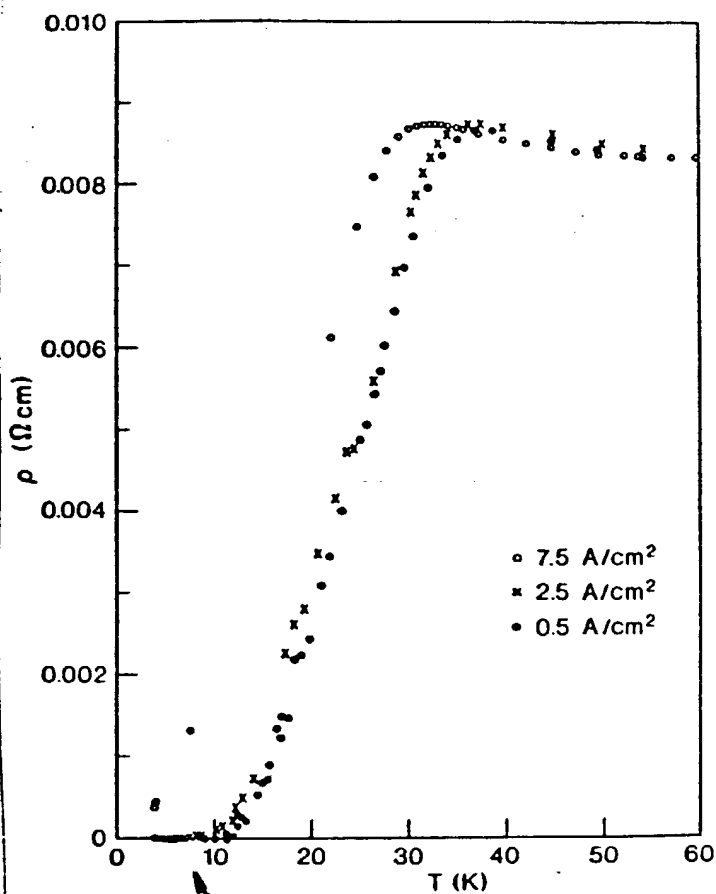


FIG. 1

$$0.008 \times 10^6 \mu\Omega \text{ cm} \times \frac{1}{1000} = 8 \mu\Omega \text{ cm}$$

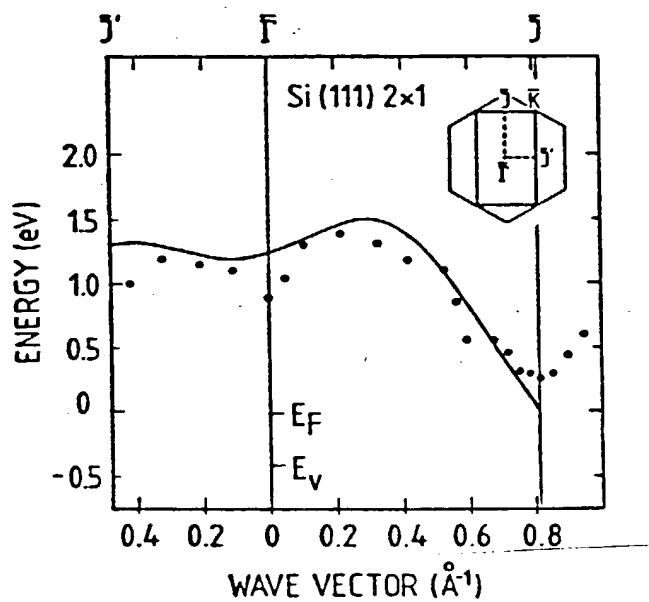


FIG. 2

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Date: 6 October 1986, 15:37:18 EDT From: RGREENE at YKTMVZ To: KAM at ZURLVM1

Alex;

Have you made any decision on my proposed specific heat experiment? I am anxious to try it. I think I can do it rather quickly after getting some samples. It may be difficult to see the transition near 30K because of a large phonon background but at the very least we could get a good estimate of the electron density of states and the Debye phonon contribution. Once I have a good specific heat between 2K and 40K I can make a better effort to resolve the electronic effect at  $T_c$  if it is small....I think I can see a 1% effect if the transition is not too smeared in temperature. Perhaps you would like to come to Yorktown and work with me on this experiment? Let me know. Best regards.

Rick

P.S. This is a good time for me to do some experiments on your exciting new compound since I am not heavily involved in other projects yet. I could get access to tunneling and neutron scattering equipment which would be very useful for seeing which phonons (if any) are involved in causing such a high  $T_c$ .

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Date: 14 October 1986, 10:42:19 EDT From: RGREENE at YKTMVZ To: KAM at ZURLVM1

Hi Alex:

This note is to give you my user id and node on the VM system. You can see them above. When you send the samples for the specific heat experiment let me know via VM. My office at Yorktown is 02-026. I will make the specific heat my highest priority and should be able to start the experiment as soon as the samples arrive. I will keep you informed on the progress of the experiment.....it will probably take a few weeks to get reliable data assuming there are no unexpected problems.

As I said on the telephone you can ignore the sample dimensions sent to you by my manager C. Tsuei. He did not talk to me before sending you his VM note and he did not understand the requirements of the specific heat apparatus. What I need are samples to cover an area of 2mm x 2mm on the bolometer. Some extra samples will also be necessary in case we break or lose the primary samples. It would be best to not compress the samples or bind them together with any foreign materials which could alter the specific heat.

Best Regards,

Rick

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Date: 15 October 1986, 15:02:34 EDT From: RGREENE at YKTMVZ To: SANDRO

Sandro; I have a court at 5pm. Do you want to play?

Rick

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Date: 16 October 1986, 09:06:42 EDT From: RGREENE at YKTMVZ To: GGRIN



I'm thinking about taking my son to Mohansic tomorrow afternoon around 1:30. If you want to join us let me know.

Rick

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Date: 16 October 1986, 13:27:32 EDT From: RGREENE at YKTVMZ To: JBMART

The reference is PRL 57, 1177(1986). I think a pressure experiment might be interesting. Let me call Chaikin and Brian first then I'll get back to you.

Rick

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Greene

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Date: 20 October 1986, 08:51:36 EDT From: RGREENE at YKTVMZ To: LOUGHRAN at ALMVMC

Hi Diane;

Starting to get cold around here but at least the sun is shining. Hope all is well with you. You can discard the Chaikin-Greene manuscript. It's been published and I have the reprints. Thanks for forwarding any remaining mail that comes to Almaden.....it takes a long time for scientific types to know when one has moved. I'll be seeing you in Jan.

Regards,

Rick

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Date: 20 October 1986, 15:18:13 EDT From: RGREENE at YKTVMZ To: KAM at ZURLVM1

Alex;

The samples have arrived. They are bigger than I expected and all appear to be compressed pellets. Before I start on the specific heat I need to know a few things.

1. What is the difference between the samples marked I(red) and II(black)?
2. Have the samples been compressed with any foreign material, such as a binder?
3. Can the samples be cut without falling apart? If so do you recommend using a string saw or a razor blade or something else? Will water damage them?

4. Has the magnetic susceptibility been measured on any of these samples or on other samples from the same batch? I may want to measure the resistivity or susceptibility on these particular samples to make sure they exhibit the behavior you found before spending a big effort on the specific heat.

We are measuring the background specific heat of our apparatus up to 40K tomorrow...hopefully by the end of the week we will begin your samples so please call or send me via VM the answers to the above questions as soon as possible.

Best regards,  
Rick

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Rick

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Date: 23 October, 1986, 13:43:17 EDT From: RGREENE at YKTVMZ To: BED  
at ZURLVM1 cc: KAM at ZURLVM1

Hi George , Alex;

Just a note to keep you informed of our progress. We are almost finished with the background specific heat. Tomorrow we will mount a 25mg slice of your sample BLC02....it should take about a week to get the data in the earth's magnetic field. It probably will be necessary to also measure the specific heat in a magnetic field to accurately determine the superconducting contribution. Do you have any data on the critical field for this sample...if not we can measure it ourselves. Also I need to know if the samples you sent me are each a single phase....from your x-ray studies. I haven't received your preprint yet....perhaps some of my questions are answered there.

I will be away from the lab tomorrow and look forward to your response on Monday. Best regards.

Rick

---

Date: 23 October 1986, 14:00:11 EDT From: RGREENE at YKTVMZ To: MALOZEM

Alex;

Sorry I haven't gotten back to you but I have been very busy with two exciting experiments....the specific heat of the new Zurich high

temperature superconductor and the 2D melting X-ray experiment with Paul which finally looks like it will work. I'm not really sure if there are any easily defined X-ray experiments that can be done to prove or disprove the nice model you presented this morning but I will think more about this. However given my present experimental commitments it will be a few months before I could realistically do anything. Keep me informed. Thanks.

Rick

---

Date: 23 October 1986, 14:27:22 EDT From: RGREENE at YKTMVZ To: BED at ZURLVM1

George; Thanks for the Susceptibility info. I'm glad that I chose BLC02 I for the first experiment. How wide in temperature is the para-diamagnetic transition in this sample? Regards.

Rick

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Date: 23 October 1986, 18:58:35 SET From: j.g.bednorz  
BED at ZURLVM1 To: RGREENE at YKTMVZ

Hi Rick

Here are the results of our susceptibility measurements, done on the samples You got from me. I'll give You the temperatures where the para- to diamagnetic transition occurs.

|                |                 |
|----------------|-----------------|
| BLC02 I 32K    | BLC02 II 26-27K |
| BLC08 I 13-14K | BLC08 II 25-26K |
| BLC021I 25K    | BLC021II 27-28K |

So You don't need to involve somebody else with these measurements, which I prefer doing myself here.  
While typing this, I got the message that You send a note.

Salu  
George.

---

Date: 23 October 1986, 16:00:52 EDT From: RGREENE at YKTMVZ To: TFHEINZ

Tony;

I can't serve on the colloquium committee this year. I'll try to think of possible speakers however. Sorry and thanks for thinking of me.

Rick

---

Date: 23 October 1986, 17:32:09 EDT From: RGREENE at YKTMVZ To: GRANT at ALMVMC

Hi Grant;

Where have you been hiding? I need to talk to you since you didn't answer my last note. I'll be here on Monday..try me then.

the old boss

YKTVMZ To: VERMLI

at Yorktown. Thanks and regarus.

Rick

Date: 27 October 1986, 08:32:34 EST From: RGREENE at YKTVMZ To: GGRIN

Got your note too late.....sorry I missed the big game. Let's try the  
~~at the same time day. I won't have time for a real golf game for a~~

Date: 28 October 1986, 17:30:52 EST From: RGREENE at YKTVMZ To: BED  
at ZURLVM1, KAM at ZURLVM1

Hi George, Alex:

Did you get the last two notes that I sent you? I'm measuring BLC02 this week...nothing definitive yet. I'll keep you informed. What is the critical field of this sample? Is BLC02-I all the same phase? I haven't received your preprint yet...have you sent it? Best regards.

Rick

Date: 29 October 1986, 17:20:53 EST From: RGREENE at YKTVMZ To: GGRIN

Hey Rod;

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Date: 29 October 1986, 16:41:22 SET From: j.g.bednorz  
BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick,

Sorry for letting you wait so long to get an answer. Alex told me that he sent the reprint already 10 days ago. I have sent you a second one today, in case the letter got lost somewhere.

Concerning your questions:

From our measurements we can tell you that the critical field  $H_{c2}$  is higher than 1.5 kG.

Now about the phases present in our samples:

|          |           |                          |                |
|----------|-----------|--------------------------|----------------|
| BLC02 I  | 3 phases: | °cub. perovskite/tetrag. | perovskite/CuO |
| BLC02 II | 2 phases: | " /                      | " /---         |
| BLC08 I  | 2 phases: | " /                      | " /---         |
| BLC08 II | 1 phase : | -----/                   | " /---         |
| BLC021I  | 2 phases: | "                        | " /---         |
| BLC021II | 1 phase : | -----/                   | " /---         |

Best regards also from Alex

George.

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Date: 30 October 1986, 09:20:04 EST From: RGREENE at YKTVMZ To: GRANT  
at ALMVMC

Hi Grantie;

I'm here ..where are you? Don't even have a phone answer any more. How come you didn't answer the questions in my last note.

As for the 3M meeting I am supposed to share a room with Torrance starting Sunday nite. I'm not sure if he's still coming or how long he's staying. Check with him and you can share the room with us or replace him. Let me know.

Greene

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Date: 30 October 1986, 09:31:20 EST From: RGREENE at YKTVMZ To: BED  
at ZURLVM1, KAM at ZURLVM1

Hi Alex and George:

I just tried to reach you by telephone without success so here is a note. We have measured the specific heat(C) of BLC02-I from 2-40K...the analysis is not yet complete but the preliminary data does not show any bump in C near or below 32K. However at this stage we could only see a bump or jump if it was greater than 10% of C so more accurate ex-

periments will be required. Since BLC02-I is a 3 phase sample it was not a good choice for the measurement since I will not be able to analyze the data for density of states and Debye Temp. Do you know how much of each phase is present in this sample? Also is the cubic perovskite a metal or insulator?

It would be better if you had some single phase single crystals of the tetragonal phase. Is this possible? We could measure samples as small as a few milligrams.

Without crystals I am planning to measure BLC08-II next since this is a single phase. Once you send me the info on the chemical composition and structure of this phase I can analyze the data and hopefully get results that we can publish. The measurements will take another week if all goes well. If we have to put on a magnetic field this will take several more weeks... specific heat data is tedious to obtain and analyze even with a computer.

Please answer the above questions as soon as possible. I am still waiting for your preprint...the first one must have gotten lost. Did you send it by external mail? Best regards.

Rick

---

Date: 30 October 1986, 18:30:43 SET From: j.g.bednorz  
BED at ZURLVM1 To: RGREENE at YKTMZ

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Hi Rick,  
BLC021III or BLC08II would be good to try.  
BLC021III shows a more pronounced resistivity drop, as compared to the sample I. BLC08II I could not check till now.  
The composition is  $\text{Ba}_{0.15}\text{La}_{1.85}\text{CuO}_{4-x}$  and  $\text{Ba}_{0.10}\text{La}_{1.90}\text{CuO}_{4-x}$  respectively. The structure of  $\text{La}_2\text{CuO}_4$  is a layered perovskite of  $\text{K}_2\text{NiF}_4$  type.  
The pure material is orthorhombically distorted. Exchanging La by Ba is leading, as we believe, to the formation of a tetragonal unit cell.  
Our powder diffraction pattern can be indexed with a bodycentered lattice and  $a=3.79\text{\AA}$  and  $c=13.21\text{\AA}$  for  $x\text{Ba}$  around 0.1. For crystals with  $x\text{Ba}=0.02$  I also checked the lattice parameters by single crystal precession experiments. But here we already have the problem. These crystals have been obtained from powders with  $x\text{Ba}=0.1$ , so we have to expect segregation and it will take a while, to get the crystals with a composition where the resistivity drop is observed in the powders.

To your question about the cubic perovskite, it shows metallic conductivity as well.  
I really hope, that you get the preprint very soon.

Best regards George.

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Date: 30 October 1986, 15:06:11 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1

George; Thanks for your quick answer to my questions. I forgot to ask you if you know the relative weight % of the 3 phases in sample BLC02-I. If so I may still be able to get some useful information from the data we have taken so far.

I also just realized that you could send me the preprint via VM assuming it was typed on line. Please see if your secretary can do this. Thanks and regards.

Rick

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Date: 3 November 1986, 16:58:28 EST From: RGREENE at YKTVMZ To: JERRY at ALMVMC

Hi Jerry;

All is set for our room at the Hyatt starting Sunday nite the 16th. I'm not sure when I'll arrive but they have your name attached to the room also and it's guaranteed for late arrival. See you there. I saw some article recently about an organic ferromagnet....I think in JETP letters. Do you know about that work?

Rick

---

Date: 4 November 1986, 17:00:53 EST From: RGREENE at YKTVMZ To: SANDRO

I cannot play tomorrow...sorry.Next week.If I can change my schedule tomorrow I will call you in the morning.

Rick

---

Date: 11 November 1986, 10:04:02 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1

Hi George;

No I have not given up...in fact I just tried to reach you by phone.My terminal is not working since I just changed my office so It may take me a little longer to respond to messages.

At any rate I have finished the specific heat measurement from 4-35K in zero magnetic field. It will take a few days to finish the data analysis but there is no obvious bump in the specific heat indicating superconductivity. This is not really too surprising given the very broad transition you have found in resistivity and susceptibility.

I expect to get some useful information from the data anyway but for this I need the exact composition of BLC021-II.Is it Ba<sub>1.5</sub>La<sub>1.85</sub>CuO(4-.15)? Please send this as soon as possible by VNET....I will get back to you and Alex later with more info. Regards.

Rick

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Date: 12 November 1986, 09:19:56 EST From: RGREENE at YKTVMZ To: GRANT  
at ALMVMC

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Greene

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Date: 13 November 1986, 13:54:49 EST From: RGREENE at YKTVMZ To:  
MALOZEM

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Alex;

I'll be happy to talk about the prospects of using magnetic X-ray scattering for thin films and interfaces. It will only be a summary of what has been done and my thoughts on what else could be done. The rest of your proposed program looks great. It's a good idea to have such an internal meeting.

Rick

---

Date: 14 November 1986, 10:17:09 EST From: RGREENE at YKTVMZ To: BED  
at ZURLVM1, KAM at ZURLVM1

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Hi Alex and George;

I will be away from the lab until 24 Nov. so I thought I would let you know the present status of the specific heat (SH) experiment and my future plans.

So far we have measured BLC021 from 3-35K. There is no evidence for a bump in SH anywhere....to a 5% accuracy. I have analyzed in detail the data between 3-10K. Here the SH is linear on a  $C/T$  vs  $T^2$  plot. The intercept gives a value for gamma of 5.9 mj/mole-K<sup>2</sup>. This is a rather large value compared to other metals and suggests that most of the BLC021 sample is in the normal state. However to be sure of this we must measure the sample in a magnetic field large enough to suppress the superconductivity. This we will start while I am away. Also we must run a test sample such as copper or silicon to know the accuracy of our gamma determination. All this will take 2-3 more weeks. As you see it takes considerable effort to do a reliable specific heat measurement which makes it very important that we have well characterized, single phase samples. As we discussed yesterday George it may be better to do the SH experiment on a bunch of single crystals if you can prepare them. Five mg of material should be enough to get reliable data.



We will also measure the critical field up to 9T via resistivity. I want to do this first so I have some idea of the field necessary to get the normal state at 3K....our SH apparatus has a field of 5T maximum.

I'll talk with you when I return. I am still quite excited about these new materials and hope that we can continue to collaborate on various experiments even if the specific heat does not give evidence for bulk superconductivity. I should remind you that it took many years of work before the BaPbBi Oxides were shown to be bulk Superconductors.

Best regards,  
Rick

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Date: 25 November 1986, 09:43:48 EST From: RGREENE at YKTVMZ To: PARKIN at ALMVMC

Hi Stuart;

Thanks for your note. I haven't heard from Helmut but he is probably very busy starting his new job. Haven't heard about the Japan proceedings either.....are you still interested in organic metals? What is happening with your work on thin films? I expect to be out to San Jose sometime in January and you can bring me up to date.

Until then I am very busy with X-ray scattering and some other experiments on new inorganic materials. Have a good holiday season.

Best regards

Rick

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Date: 25 November 1986, 10:35:50 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1, KAM at ZURLVM1

Hi Alex and George;

I have returned from my trip and will once again start work on your new superconductor. This week is the Thanksgiving holiday so not much will happen until next week. The specific heat apparatus is now modified to make measurements in a magnetic field....however we must first calibrate and check that it works with some known material.

Please tell me what is happening with your studies of time dependent effects. Is the sample BLC021 still good....we have not yet measured the resistivity in a field as a function of T but we plan to along with the specific heat experiment. Perhaps you should send me some new single crystals for the next experiment.....I don't want to waste time on a bad sample.

I would like to send an abstract to the March APS meeting on the specific heat results. Is this agreeable with you? The abstracts are due the end of next week (Dec.5) so let me know soon. At this stage there is not much definitive to say but I can still write a general abstract about specific heat and I'm sure I will have definitive results by the time of the meeting.

Best Regards,  
Rick

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Date: 26 November 1986, 09:56:43 EST From: RGREENE at YKTMVZ To: KAM  
at ZURLVM1

Hi Alex;

Are you sending your susceptibility preprint to people outside of IBM? If so Ted Geballe at Stanford would like a copy...he saw your paper in Z.Physic and called me to see if I knew about your work.

I can send him a copy if you are agreeable. Please let me know about this and more importantly the answer to my note of yesterday.

Best regards,

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DO115

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Date: 1 December 1986, 17:31:01 EST From: RGREENE at YKTMVZ To: KAM  
at ZURLVM1, BED at ZURLVM1

Hi Alex and George:

Here is a draft of the abstract that I would propose submitting to the APS March meeting. Please make any changes or comments and let me know today. I look at this as a way to publize your work in the USA and to present whatever specific heat results are obtained by March.

#### POSSIBLE HIGH $T_c$ SUPERCONDUCTIVITY IN THE Ba-La-Cu-O SYSTEM

We report measurements on new oxide superconductors of the composition  $\text{La}(2-x)\text{Ba}(x)\text{CuO}(4-y)$  with  $x \ll 1$  and  $y > 0$ . Polycrystalline samples with  $x = .15$  show a resistivity drop of three orders of magnitude and a transition from Pauli paramagnetism to diamagnetism with an onset temperature between 30-35K. (ref 1 and 2....your two papers). The transition is complete by 10K and magnetic field studies suggest superconductivity of a percolative or granular nature. Our specific heat experiments indicate a large electron density of states but no evidence of a sharp jump near  $T_c$ ---consistent with the small Meissner signal observed (2% of complete flux expulsion) and the broad transition width. These measurements, along with X-ray and critical field results, will be analyzed for the possibility of high  $T_c$  superconductivity in these new oxide materials.

The authors would be the three of us and Steve VonMolnar (whose apparatus I am using)....possibly I would add Al Torresen (Steve's assistant) without whom the specific heat experiments could not have been done.

The abstract could perhaps be a bit longer but there may not be much space after the authors and references are included.

Regards,  
Rick

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Date: 2 December 1986, 09:17:12 EST From: RGREENE at YKTMVZ To: KAM  
at ZURLVM1

Alex;

I scheduled your seminar for 8 Jan at 3:30pm....this was the only time I could get a room. Please send me a title and short abstract so I can get it on the lab calender as soon as possible. Do you need a hotel reservation? Regards.

Rick

P.S. Plan on saving some time on 9 Jan. to discuss our specific heat data. If you would like to go out together for dinner on the 8th let me know.

---

Date: 4 December 1986, 10:48:02 EST From: RGREENE at YKTMVZ To: BED  
at ZURLVM1

Hi George;

I just tried to telephone you. I am measuring the resistance and critical field of sample BLC0-21. So far it reproduces the data in your Z. Physik paper...I don't see a bump except perhaps near 25K (but I need to take more points). The surprising thing is that a small field (1000 Oe) increases the Resistance to the value at 25K but at higher fields (up to 7Tesla) there is almost no more change in R. Tell you more when I have more data.....so far it suggests that doing the specific heat in low field will be useful.

Would you please send me whatever info you have on the structure of the superconducting phase i.e. a picture and a powder X-ray that gives the Bragg peak positions.

What have you learned about the time changes in these samples? I would like some fresh single phase samples for our next specific heat experiment...to begin at the end of next week. If you have single crystals that would even be better....but I realize this is a difficult problem

regards,

Rick

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Date: 5 December 1986, 10:56:34 EST From: RGREENE at YKTVMZ To: ORR

OK. What are you up to? Drop in and see me sometime in vonMolnars lab.

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Rick

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Date: 5 December 1986, 11:10:42 EST From: RGREENE at YKTVMZ To: KAM  
at ZURLVM1, BED at ZURLVM1

Hi Alex and George:

I'm getting some good critical field results now although I still don't totally trust my contacts. The resistance vs. temp. follows your data but there seems to be two superconducting regions (perhaps 2 phases)... one below 22K and the other below 33K. The critical fields are very different in these two temperature ranges. The good news is that I am getting a critical field vs temp curve between 20-30K and this will allow me to estimate gamma to compare with the specific heat gamma. Incidentally the critical field at 4K is greater than 7Tesla (as expected for a high Tc material) so we may eventually want to go to the MIT magnet lab to measure it better.

The specific heat exp. is progressing nicely and we will be finished with all our calibrations next week. What sample do you recommend that I use based on your recent work?

As soon as I have collected and plotted all the critical field data I will send you a figure along with the abstract to the March meeting.

Best regards,  
Rick

P.S. Please send me whatever info you have on the structure of the SC phases.

I am giving an internal journal club seminar on your resistivity and susceptibility papers.

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Date: 8 December 1986, 09:26:48 EST From: RGREENE at YKTVMZ To:  
LOUGHRAN at ALNVMC

nappy holidays....see you in Jan (maybe)

Rick

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Date: 3 December 1986, 16:39:02 SET From: KAM at ZURLVM1 To: RGREENE  
at YKTVMZ

Rick, here is the title and abstract for my seminar :

'Superconducting and Structural Properties of the BaLaCuO System'

Resistivity and susceptibility measurements as well as x-ray powder analysis carried out at the Rueschlikon laboratory will be described. The electric and magnetic data indicate the existence of a percolative superconductor with onset above 30 K. The newest magnetisation measurements as a function of temperature and field prove the presence of a superconductive glass. The highest  $T_c$  samples correlate with an orthorhombic-tetragonal structural phase transition.

please check for the english, thanks

Alex

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Date: 9 December 1986, 10:29:48 EST From: RGREENE at YKTVMZ To: GGRIN

Let's stick to our Weds tennis.....4;30 right?

Rick

---

Date: 9 December 1986, 10:31:06 EST From: RGREENE at YKTVMZ To: POMERAN

Mel;

I can't take the court on Thurs. so why don't we just put off our game until next week.

Rick

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Date: 9 December 1986, 10:37:27 EST From: RGREENE at YKTVMZ To: BED  
at ZURLVM1, KAM at ZURLVM1

Hi George , Alex;

Thanks for your note George. I will send you the Critical field data today. It seems to reproduce your low field results and has the data up to 7Tesla....I could go to 9T but will do that later. I assume from your note that you think that BLC021 is still a single phase...is that correct? I will use this sample for the specific heat in a magnetic field.

I am a little puzzled by the critical field data...it suggests that your susceptibility data was measuring the superconductivity that occurs below 20K and the superconductivity above 20K may not be a bulk effect. It's also a little disturbing that I measured such a large linear term in the specific heat in earth field.....the measurements at 5T should clarify this however.

Can you tell me the density of the SC phase? I need this to estimate gamma from the critical field slope. Also what is your estimate of the value of the resistivity just above Tc? I assume a single crystal would be at least 10 times lower. Also I would like to know your estimate of the Pauli susceptibility above Tc from your data....this will give another estimate of gamma.

Thanks for sending me your info and figures of the structure..I hope it arrives before next Tuesday.

Best regards,

Rick

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Date: 9 December 1986, 11:32:57 EST From: RGREENE at YKTVMZ To: MALOZEM

I don't know Creuzet that well but he seems to have done some good work and seems to know what he's talking about. I'm not sure how independent, creative or hardworking he is. What would he be doing here? How closely working with an RSM? Who with?

Rick

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Date: 9 December 1986, 14:34:51 EST From: RGREENE at YKTVMZ To: POMERAN

Mel;

OK for Monday. SEe you there unless you hear otherwise.

Rick

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Date: 8 December 1986, 18:56:40 SET From: j.g.bednorz  
BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick Sorry that you had to wait for the answer since Thursday. I've been in Germany since Friday. In November I told you on the phone, that something happened to that sample BLC021II which I measured again one month after the first resistivity run. The resistivity curve showed a peak at 34K and a shoulder occurring around 25K after a 60 percent drop. At that time I was also surprised about the magnetic field dependence in the low temperature part. The resistance was increased by fields between 0-0.4 Tesla but seemed to saturate at values above, whereas the field dependence of the peak at 34K was smaller. It would be good to compare our results, especially as you have the possibility to go to higher fields than 0.7 Tesla, which is the limit for our resistivity system. Unfortunately I do not see the occurrence of a new phase related to the appearance of that shoulder in the resistivity.

Concerning your internal seminar, I will send you an X-ray powder spectrum and the structure of La<sub>2</sub>CuO<sub>4</sub>, which I've drawn already, using the information given in a German article. You can even have the viewgraphs. We should discuss questions about the structure at the phone.

Best regards  
George.

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Date: 9 December 1986, 18:47:08 SET From: j.g.bednorz  
BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick,

Thank you for your quick answer. I just discussed with our Japanese guest Masaaki Takashige, who is involved in the susceptibility measurements. First of all you should not be worried about the susceptibility data shown in the preprint, because the samples shown there are not single phases. You will see from the X-ray pattern that the amount of the foreign phase can be very large, greater than in BLC021 I. Single phase means, that in the X-ray diagrams we only can detect the La<sub>2</sub>CuO<sub>4</sub>:Ba. The small susceptibility could indicate that only parts of that phase is superconducting, for instance an intragranular network. That is the reason, why we think the density of La<sub>2</sub>CuO<sub>4</sub> (from the X-ray data = 7 g/ccm) would not lead to a correct estimation in your case. The Pauli susceptibility

of sample BLC021II, this sample is not shown in the paper, shows a field dependence close to  $T_c$ , this dependence is getting weaker with increasing temperature, and we expect it to vanish 10 or 20 degrees higher, but in case of this sample it has not been confirmed. I'll give you values at 32-33K for the mass susceptibility:

0.3 Kgauss 1.28 E-7 ccm/g

5.0 " 1.35 E-6 ccm/g

10.0 " 1.61 E-6 ccm/g Especially for the low field value

we have to be aware of a large error.

For the resistivity value: My measurement (second one, where I realized the magnetic field dependence) showed a peak value of  $7.36 \text{ E-3 Ohm cm}$ .

Concerning the results of the Japanese group: Do you know more about it? How did they measure the 40% Meissner effect, did they measure ac or dc? Is something known about the magnetic field they applied? I think they believe the metallic perovkite phase is responsible for the superconductivity, whereas we found that the single phase samples containing  $\text{La}_2\text{CuO}_4:\text{Ba}$  in the powder diffraction pattern, show the highest susceptibilities. You will get the copies of the results as soon as they are plotted.

Best regards

George. can be very large, larger than  
in BLC021. Talking about single phase samples

les,

---

Date: 10 December 1986, 10:48:47 EST From: RGREENE at YKTMZ To: GRANT  
at ALMVMC

I haven't forgotten you....just busy as hell with this 30K superconductor  
and can't think about anything else. Happy Holidays Turkey.

Looks like I won't have time to ski...too much physics to do.

le

Greene

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**College Ruled White Paper**  
**Single Subject**

Danbury, N. H. 06825

601-253-9816

601-253-9816

12/1/86

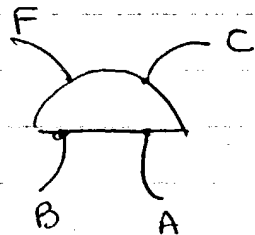
Resistivity of BLCO-211 in Steve's  $H^3$  Rig

Check out PAR first - usual diff input wry  $R_{ind} \approx 200k$

Using  $100\Omega$  R gives  $V = 1mV \Rightarrow I = \frac{10^{-3}}{100\Omega} = 10^{-5}$  Amps  
 $= 10\mu A$

$$\frac{2}{5} = \frac{1}{2.5}$$

### Sample Setup



sample has non uniform thickness  
 In contacts - 1mil Cu wires

At Room T

### DC 2 probe

$$AB = 100\Omega$$

$$AF = 88\Omega$$

$$AC = 88\Omega$$

$$BF = 72\Omega$$

$$BC = 73\Omega$$

$$FC = 62\Omega$$

### Do AC 4 probe (22 Hz)

$$I = 10\mu A \text{ thru } AB$$

get  $12\mu V$   $90^\circ$  out of phase

$$\Rightarrow 1.2\Omega$$

I thru FC get  $12\mu V$  on AB  $90^\circ$  out of phase

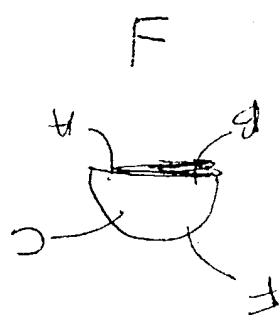
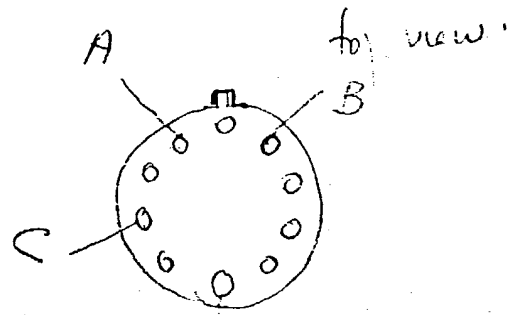
I thru FB get  $12\mu V$  on AC " " "

I thru FA get  $12\mu V$  on BC in phase

go to 50Hz and get in phase signal  
 with  $\sim 80m\Omega$  resistance

Doesn't look good but let's try it any way  
 and use LR-400 bridge

DO NOT THROW AWAY



DC  
AB = 100  
AF = 85  
AC = 85  
BF = 72  
BC = 73  
FC = 62

12 # of 7g  
Sample

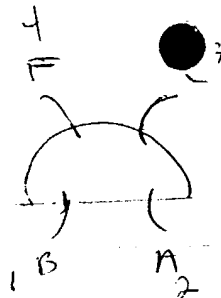


At Room T - 4 probe

$$R_{FC} = 75.6 \text{ m}\Omega$$

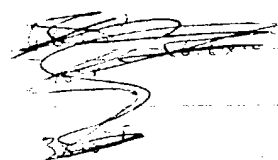
$$R_{AB} = 44.4 \text{ m}\Omega$$

$$R_{BF} = 7.4 \text{ m}\Omega \rightarrow \text{changes with excitation voltage} \\ \text{+ } \Omega \text{ scale}$$



Cool down sample anyway using LR-400 to measure  
AC Bridge  
( $\nu = 16 \text{ Hz}$ )  
 $R_{FC}$

| $R_{ADZ}$ | T       | $R_{FC} (\text{m}\Omega)$ |
|-----------|---------|---------------------------|
|           | 300 K   | 76.0 mΩ                   |
|           | cooling | $R$ is dropping           |
|           | ?       | 73.22                     |
|           | ?       | 70.00                     |
|           | ?       | 66.5                      |
| 1059      | ?       | 63.7                      |
| "         | —       | 60.45                     |
| 1060      |         | 58.87                     |
| 1061      |         | 57.36                     |
| 1065      |         | 49.0                      |
| 1074      |         | 46.0                      |
| 1087      |         | 49.0 ← minimum            |
|           |         | 55.0 ← get small          |
| 1260      |         | 0.4 mΩ                    |
| 1340      |         | 0.32                      |
| 1115      |         | 21.1 mΩ                   |
| 1165      |         | 0.12 mΩ                   |



1 ma

$$J = \frac{10^{-3}}{.2 \times .2}$$

$$= \frac{1}{4} \times 10^{-1} \\ = .025 \text{ A/cm}^2$$

2 probe dc at 4K

$$FC = 99 \Omega$$

$$AB = 158$$

$$AC = 147$$

$$AF = 142$$

$$BF = 118$$

$$BC = 118$$

Heat Sample pt by pt with  $H=0$

| $R_{uO_2}$      | Ge            | T     | $R_{FC}(m\Omega)$ | Comments   |
|-----------------|---------------|-------|-------------------|--|
| 1240 $\Omega$   | 650 $\Omega$  |       |                   |  |
| 1336 $\Omega$   | 1034 $\Omega$ | 4.2 K | $0.15 \pm .01$    | 0.06 Ext, .2 Range $\Rightarrow I=300 \mu A$   |
| 1326 $\Omega$   | 885           | 4.8 K | $0.15 \pm .01$    | "  |
| 1306            | 779           | 5.5 K | 0.15              | "  |
| 1255            | 593           | 8 K   | 0.14              | "  |
| 1203            | 490           | 11. K | 0.14              |  |
| 1174            | 361           |       | <del>0.18</del>   |  |
| 1172            | $480 \pm 2$   | 13. K | 0.14              | Still not regulating well<br>$\pm R_{uO_2} = 1170 \Omega$<br>takes ~ 5 minutes to come<br>to equilibrium<br>Does not regulate well<br>here |
| 1153            | $303 \pm 1$   | 17 K  | $0.74 \pm .02$    |  |
| $1135 \pm 2$    | $176 \pm 5$   |       | $9.0 \pm 1$       |  |
| <del>1133</del> |               |       |                   | <del>Substrate to 412 gas</del>  |

May have too much gas in  $He^3$  chamber - lower Sub T

12/3/86

5

Run as  $f(H)$  at 4.2 K

$$\left. \begin{array}{l} 2 \text{ mV/mmp} \\ \end{array} \right\} 0.0695 \text{ T/mV}$$

~~812~~

Let's Run as  $f(T)$  again with  $H \approx 0$  — not quite zero because  
 removed field after  $H$   
 sweep remains

→  $I = 300 \mu\text{A}$ 

| $R_{\text{NiO}_2}(\Omega)$ | Ge-28387          | T     | $R_{\text{FC}}(\text{m}\Omega)$ | Comments   |
|----------------------------|-------------------|-------|---------------------------------|--|
| 1155.5 ± 3                 | 402 ± 1 $\Omega$  | ~14.5 | 11.8 ± 0.1                      | Set at 10.9 — 0 mbar<br>gas in SVC   |
| 1130                       | 200 ± 20 $\Omega$ | ~20 K | 17.8                            | Not stable $T$ — each<br>good to ± 20 mK<br>Set back at 16 K<br>30 mbar $\text{He}^3$ pressure |
| 1096                       | 26 $\Omega$       | 42 K  | 53.4                            | } quasi equilib. — no<br>heat<br>sample cooling<br>slowly from 42 K                            |
| 1097                       | 28.3              |       | 53.8                            |  |
| 1099                       | 31.7              |       | 54.4                            |  |
| 1100                       | 34.1              |       | 54.7                            |  |
| 1101                       | 37.2              |       | 54.9                            |  |
| 1103                       | 40.5              |       | 55.0                            | ← this is maximum — start<br>to decrease   |
| 1104                       | 45.0              |       | 54.6                            |  |
| 1105                       | 48.0              |       | 53.9                            |  |
| 1107                       | 55.0              |       | 50.4                            | cooling more rapidly now<br>was set pt 1.1100  |
| 1110                       | 65.0              |       | 39.0                            |  |
| 1112                       | —                 |       | 30.0                            | ← not good equilib.  |
| 1120                       | 113               |       | 19.5                            |  |
| 1119                       | 100 ± 3           |       | 20.0                            | ← trying to stabilize with set<br>pt 1.1200  |
| 1126                       | 150               |       | 15.0                            | not so good  |
| 1130                       | 175               |       | 10.7                            |  |
| 1132                       | 181               |       | 9.4                             |  |
| 1138                       |                   |       | 5.0                             |  |
| 1141.7                     | 256 ± 3           |       | 3.0 ± 0.2                       | Wait 20 min for stable pt<br>Set at 1140 — not that<br>stable                                  |
| 1152 ± 1                   | 330 ± 3           |       | 0.45                            | quasi stable set pt<br>1150  |

| $R_{H_2O_2}$     | Ge           | T            | $\frac{1}{2}$ RFC | Comment              |
|------------------|--------------|--------------|-------------------|----------------------|
| $1177_5 \pm 0.5$ | $469 \pm 12$ | $\sim 12.5K$ | $0.14$            | <del>is</del> stable |

Put on H field now

He boiling off rather rapidly — because sorb at 16K  
and gas in SVC

try this tomorrow with gas pumped out of SVC

Put sorb back at 3K, He<sup>3</sup> p ≈ 0

12/4/86

Run some more T's and H's

I = 300ua

| STK   | $R_{D2}$ (V <sub>eff</sub> ) | Ge 121       | T (K) | $R_{FC}$ (m $\Omega$ ) | Comments   |
|-------|------------------------------|--------------|-------|------------------------|--|
| 1.140 | 1.142 <sub>3</sub>           | 306 $\pm$ 1  | 17.0  | 3.55                   | Sub 12.4K - no obvious P of He <sup>3</sup>                              |
| 1.137 | 1.139 <sub>5</sub>           | 283 $\pm$ 1  | 17.5  | 10.5 $\pm$ 1           | Very stable Pt - settings 507035 on left                                 |
| 1.135 | 1.137 <sub>5</sub>           | 264 $\pm$ 1  | 18.0  | 11.9                   | small remanent H field causes a problem here but T is very stable        |
| 1.132 | 1.134 <sub>0</sub>           | 236          | 19.0  | 13.5                   | Run field between these two pts (see full run ①)                         |
| 1.128 | 1.131 <sub>2</sub>           | 209          | 19.8  | 14.73                  |  |
| 1.125 | 1.126 <sub>2</sub>           | 161          | 21.8  | 17.0                   |  |
| 1.120 | 1.120 <sub>7</sub>           | 121          | 23.9  | 19.4                   | By slowly increasing set pt we get very stable pts with this sub setting |
| 1.112 | 1.112 <sub>7</sub>           | 76.5 $\pm$ 1 | 28.0  | 27.0                   | quasi equilib.   |
| 1.109 | 1.111                        | 69.5         | 28.7  | 32.0                   | quasi stable   |



12/5/86

Some More — Sub at 12.6k

T Reg. settings 50, 20, 30

$I = 300 \mu A$  mLR-400  
 .06 Exits  
 .2V Range

| $R_{uO_2}(V_{eff})$ | $G_e(R)$ | $T(k)$               | $R_{FC}(m\Omega)$  | Comments   |
|---------------------|----------|----------------------|--------------------|--|
| 1.338               |          | 4.2k                 | 0.15               |  |
| 1.252 <sub>6</sub>  | 660 ± 1  | 6.7k                 | 0.15               | Entry to equilibrium here  |
| 1.227 <sub>4</sub>  | 596 ± 1  | 7.7 <sub>5</sub>     | 0.15               |  |
| 1.202 <sub>4</sub>  | 545      | 9.3                  | 0.35               | Is there still a small field from the Magnet? Yes                          |
| 1.177 <sub>4</sub>  | 492      | 11.5                 | 2.13               | → must be smaller  |
| 1.162 <sub>5</sub>  | 439      | 13.3                 | 5.30               | reduces to ~ 1.0 mΩ by playing with field — keep field here and continue   |
| 1.152 <sub>7</sub>  | 385      | 15.0                 | 3.0                |  |
| 1.142 <sub>4</sub>  | 306      | <del>17.0</del> 17.0 | <del>7.0</del> 7.0 | <del>not stabilizing in field</del><br>goes to 6.5 playing with field zero |
| 1.131 <sub>5</sub>  | 209 ± 2  | 19.8                 | 12.6 ± 0.3         |  |
| 1.115 <sub>7</sub>  | 92 ± 1   | 26                   | 22.5               |  |
| 1.109 <sub>8</sub>  | 60 ± 1   | 30                   | 43                 | hard to stabilize<br>Sub set at 15k  |

Try increasing current at various T's

but must worry  
about heating  
due to 200 $\Omega$   
contacts

| Ge  | T    | R (m $\Omega$ ) | I (from LR-400 setting) |
|-----|------|-----------------|-------------------------|
| 526 | 10 K | 1.65            | 300 $\mu$ A             |
|     | "    | 1.6             | 30 $\mu$ A              |
|     | "    | 1.9             | 1000 $\mu$ A            |
|     | "    | 2.7             | 3 mA                    |
|     |      | 6 <del>mA</del> | 10 mA                   |

T increasing

→ but R  $\propto$  T increasing

All this looks like increasing sample  
T via heating at contacts

Do this when we have better contacts

Estimate of Current Density

cross section  $2.8 \times 2.5 \text{ mm}^2$

I = 300  $\mu$ A

$$J = \frac{300 \times 10^{-6}}{.05} \approx \frac{1}{2} \times 10^{-2} \text{ A/cm}^2$$

R. Green-Torresen et al

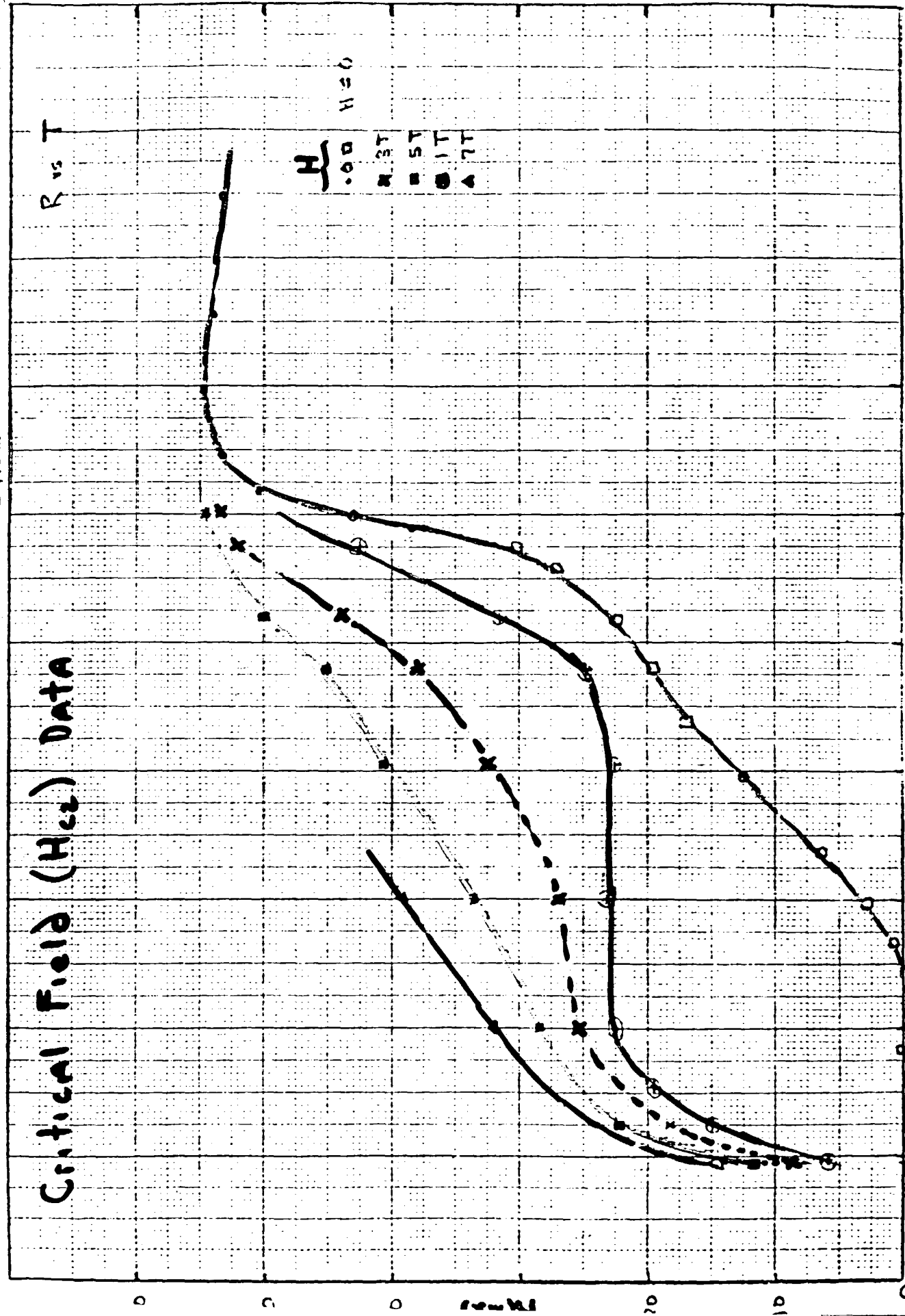
BaLaCuO<sub>2</sub> II

12/8/86

Critical Field (H<sub>c2</sub>) Data

R vs T

$\frac{H}{H=0}$   
 .00  
 .37  
 .57  
 .77



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 29, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF ALBERT M. TORRESSEN  
WITH RESPECT TO HIGH Tc SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Albert M. Torressen, hereby declare and say that:

1. I joined the International Business Machines Corporation (IBM Corp.) on June 12, 1978, and began my employment as a laboratory technician at the Thomas J. Watson Research Center, Yorktown, New York. In 1986, I was a senior lab specialist at the Watson Research center, and reported to Dr. Stephan von Molnar. My specialty has been measurement of thermal and transport properties of a material including, for example, measurements of heat capacity, resistivity, and Hall coefficients. Generally, these are dynamic measurements which serve to characterize a material.

2. On approximately October 22, 1986, Richard L. Greene approached Stephan von Molnar to enlist his assistance in obtaining specific heat measurements of samples which he said were new superconducting materials that had been received from Georg Bednorz and Alex Mueller of IBM's Zurich research laboratory. These were ceramic oxide materials comprised of Ba-La-Cu-O. In turn, von Molnar asked me to assist Greene in making these measurements, since I had expertise in the use of the apparatus and had done similar measurements for many years. I began to calibrate the apparatus and to prepare for specific heat

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measurements at that time, and worked continuously on a daily basis, from about October 22, 1986 through the remainder of 1986 and into 1987 on these measurements. Richard L. Greene was in the laboratory during these measurements and supervised the experimentation, relying on my expertise with respect to the apparatus. Later, we analyzed the data together.

3. Richard Greene wanted to do specific heat measurements of these superconducting samples. Such measurements are used to determine if a material is a superconductor and also to tell how much of the material is superconducting. In general, the specific heat of the apparatus is first carefully measured using a bolometer in order to provide background specific heat and to calibrate the apparatus. After this, the actual sample to be measured is attached to the bolometer and the specific heat of the entire apparatus, including the sample, is again measured. When the background specific heat (due to the bolometer) is subtracted, the specific heat of the sample can be determined. This is done over a temperature range, in our measurements 2-50K, in order to obtain a plot of specific heat versus temperature for the sample being measured. This is a dynamic measurement in which we look at how the heat in the sample decays as a function of time through a known heat leak and from that extrapolate via a computer program specific heat versus temperature. This is a known procedure that is done in many laboratories.

4. The commercial bolometer that Greene and I used to measure the specific heat of these superconducting Zurich samples was comprised of an insulating aluminum oxide on which strips of  $\text{RuO}_2$  were evaporated. Electrical contacts were made to the  $\text{RuO}_2$  strips, each strip having two AuCu wires attached thereto which were in turn connected to an ambient temperature control (about 2K). A heat pulse was then applied to the bolometer and its temperature decay versus time was measured. This was done over the aforementioned temperature range in order to get background specific heat and to calibrate the apparatus. Generally, it takes us about two days to measure the background specific heat in order to prepare for the actual specific heat measurements of the sample. Measurement of each sample also takes about two days, so approximately four days represents the total time required for each measurement. This is based on full time activity.

5. Prior to making the specific heat measurements, the samples are prepared. The superconducting oxide samples received from Bednorz and Mueller were pellet samples which were then cut into slices by a diamond wheel. I believe that this was done by Richard Greene. To make the specific heat measurements, a sample having a mass of about 20 mg is required, it being desirable to have a flat surface sufficient to provide good thermal contact. In the calculation of specific heat, the weight (mass) of the sample is factored into the equation. Also, I made specific checks of the measuring apparatus throughout this time period (October 22, 1986 - February, 1987) and I made continual checks on the measuring apparatus in order to ensure its calibration. All of the data collected during the measurements was also provided to a personal computer that was interfaced to the apparatus. In this manner, a computer printout of all of the measurements was available.

6. Exhibit A attached hereto is comprised of copies of eight pages of my laboratory notebook and a copy of the notebook cover entitled "Specific heat - Zurich oxide - 10/21/86". All of the writing of these pages was entered by me on the dates indicated on the pages. These pages are true copies of the corresponding pages of my laboratory notebook that I have numbered in red in the upper right hand corner to enable discussion of the data on each page. As I mentioned previously, background specific heat and calibration of the instrumentation was done prior to mounting the sample and measuring the specific heat of the sample. For example, the data on the top two-thirds of page one shows the measured data for the calibration and background measurements. The bottom of this page indicates the specific heat data that was obtained October 27, 1986 when the sample was mounted on the  $\text{RuO}_2$  bolometer. The weight of the sample is also mentioned, the sample being designated "BICO 2 - I". This stands for Ba-La-Cu-O ceramic superconductor. I noted that it was a "multi-phase sample" which is not a particular good choice for a specific heat measurement. Generally, the data is more clean and easy to interpret if the sample contains only a single phase. Measurements on the apparatus and with this particular sample continued on October 28 and 29, 1986, the data that Greene and I obtained being listed on page 2 on Exhibit A.

7. On November 3, 1986 we used a new sample, in this case the sample designated "BLCO 21 -II". We used a new calibration of the bolometer and then mounted the sample on the bolometer to take the data, which was obtained on November 4, 5, 6, 1986. The data for this sample measurement is contained on pages 4 and 5 of Exhibit A, where it is noted that this is a single phase sample. Additional data is also contained on page 6 of Exhibit A.

8. Richard Greene and I analyzed this data between about November 10 and November 19, 1986. At that time, the samples showed only a very small (1 - 2 percent) anomaly at the transition temperature, which was sufficiently small that no obvious bump occurred in this specific heat data. Because these materials had a very broad transition in resistivity versus temperature, such a very small effect was expected.

9. On or about November 19, 1986, the apparatus was changed slightly by installing a capacitor and mounting a magnet on the specific heat cryostat. The instrument was then recalibrated and measured, the data of this being shown on page 7 of Exhibit A. A capacitance bridge was used to control temperature as noted on page 8 of Exhibit A which showed further data taken on the instrumentation. After this time, we continued to take specific heat measurements of additional samples of the Ba-La-Cu-O oxide superconductors obtained from Bednorz and Mueller.

10. Exhibit B is a true copy of pages of a printout from the personal computer that was interfaced with the apparatus used to make the aforementioned specific heat measurements. These pages illustrate the background measurements and calibration of the instrumentation, as well as the data that were obtained when the sample was mounted on the bolometer. Additionally, many plots are included in this Exhibit which are plots of the data that were measured. Specific heat measurements of the samples are plotted where the samples are designated either "Zurich oxide" or "ZO". Sometimes the sample is also designated "Zurich oxide BLCO, etc." In December, 1986, additional samples were obtained from Bednorz and Mueller, these new samples containing Sr instead of Ba. They are designated "SLCO", which represents Sr-La-Cu-Oxide. The heat capacity of these samples was also measured, as represented by the plot dated January 9, 1987. Measurements were made in the absence of and in the presence of an applied magnetic field H. Sometimes the plots show

the sample plus the designation "BG". This indicates that background was also present in the measurement.

11. The data that we obtained during our specific heat measurements are representative of the type of data which we now obtain on refined samples of these superconducting copper oxide materials. At the time we made our initial measurements in 1986, we were somewhat puzzled by the small vertical offset that occurred for temperatures extrapolated from 2-0K. However, such offsets have been found to be a characteristic of the superconducting copper oxides of the type first discovered by Bednorz and Mueller.

12. In addition to his specific heat measurements, Richard Greene also measured resistivity versus temperature in the presence of a magnetic field, for these Ba-La-Cu-O samples. This was done in my lab, and I explained my experimental instruments and set-up to Greene. I observed Richard Greene making these measurements and saw the shift in resistivity versus temperature curve with an applied magnetic field. This shift clearly indicated the superconducting nature of these samples at temperatures in excess of 30°K. The measurements described in this paragraph occurred in the last week of November, 1986 and in the first week of December, 1986. These measurements and our specific heat measurements were part of our continuous daily effort, from about October 22, 1986 to establish the superconductive properties of these samples above 30°K. I recall these measurements clearly and remember Richard Greene asking me how to better stabilize the sample temperature while the applied magnetic field was changed in amplitude.

13. In addition to the acts described hereinabove relating to work done by Richard Greene and by me, I was aware of the work being done by Chang C. Tsuei to measure resistivity versus temperature for these Ba-La-Cu-O superconducting samples. I was present in the laboratory with Chang C. Tsuei and Sung Il Park during their measurement of at least one of these samples, and saw the hardcopy of a resistivity versus temperature plot developed by the xy recorder connected to their measurement apparatus. This plot showed the onset of superconductivity at approximately 35K followed by a broad transition to zero resistivity. I knew the nature of their experimentation and understood the data. This



measurement and my observation occurred approximately the first week of November, 1986.

14. My recollection of the events described hereinabove is vivid, as there was great excitement about the importance of the discovery of new superconducting materials by Bednorz and Mueller. Because of this, activity continued on a daily basis, both morning and evening, to characterize these materials in coordination with Bednorz and Mueller.

15. All acts referred to hereinabove performed by myself, Richard L. Greene, Chang C. Tsuei, and Sung Il Park occurred in the United States.

16. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Albert M. Torressen

ALBERT M. TORRESSEN

DATE: 31 March 1988

YO987-074

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 29, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF CHANG C. TSUEI

WITH RESPECT TO HIGH T<sub>c</sub> SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Chang C. Tsuei, hereby declare and say that:

1. I have a PhD in Material Science from California Institute of Technology, and worked approximately eleven years as a student and faculty member at Cal. Tech. During this time, my research was primarily on amorphous materials and superconducting materials. I joined the Thomas J. Watson Research Center of IBM Corporation in Yorktown, N.Y. in 1973 and continued my work on amorphous materials. For several years, I have been the Manager of a group in the Physical Sciences Department studying amorphous superconductivity and superconductivity of new High T<sub>c</sub> superconducting ceramic materials.

2. On approximately September 13, 1986, I returned from a sabbatical at the K. Onnes Laboratory in Holland. Upon my return, I saw a copy of an IBM activity report for May - June, 1986, in which the "novel research" of J.G. Bednorz and K.A. Mueller was described. These individuals were working in the Zurich, Switzerland research laboratory of IBM Corporation, and had observed a steep decrease of resistivity in sintered samples of Ba-La-Cu-oxides. A true copy of this activity report is attached hereto and labeled Exhibit A. On pasge 2 of the activity report the resistivity versus temperature plot is shown in Figure 1

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wherein the onset temperature for superconductivity is in the 35K range. The data and measurements discussed in the activity report were later published by Bednorz and Mueller in Z. Phys. B-Condensed Matter, 64, pp. 189 - 193 (1986), a true copy of which is attached and labeled Exhibit B. Based on my previous experience in superconductivity, I was very interested in the work of Bednorz and Mueller and discussed this work with my colleague, Richard Greene (who reported to me). I told Greene to review this activity report and to start a project on high  $T_c$  superconductors of the type described by Bednorz and Mueller. This project was started by Richard Greene and others in the group that reported to me, almost immediately.

3. I called Alex Mueller in Switzerland via telephone to request samples of his superconducting material, as well as to discuss the technical area with him. I also sent computer messages to Mueller, but could not contact him. After this, early in October, 1986, I obtained a copy of the aforementioned Z. Phys. B article by Bednorz and Mueller.

4. I knew that on approximately October 17, 1986, Praveen Chaudhari was in Zurich, Switzerland. I was told that he was given samples of the Bednorz and Mueller superconducting copper oxides to bring to the U.S. for collaborative work in the United States. I was also told that these superconducting samples were delivered to Richard Greene on or about October 22, 1986. Shortly after these superconducting samples were received, I began work to confirm the existence of high temperature superconductivity in these materials and instructed Sung Il Park to assist me. To do so, small pieces of these samples were cut by Park and Greene and were prepared with indium contact dots to which copper wires were attached. These copper wires were attached to a source of electrical current and to voltage-measuring equipment to determine the existence of the superconducting state. As the temperature of the sample was lowered, resistivity versus temperature plots were then made using standard laboratory techniques. The preparation of these samples for measurement was done by Sung Il Park, who reported to me and who was directed by me to do so.

5. A true copy of the cover sheet and a page of my laboratory notebook is attached hereto and labeled Exhibit C. On the second page of

2

this exhibit, two diagrams illustrate the samples and show the location of the indium contact dots on the superconducting samples and the numbering given to the copper wires attached to these dots. This numbering enabled us to properly connect these wires to a current source and to voltage-measuring equipment. All entries on this notebook page were made by me. The samples are generally designated by their composition, the term "BLCO" standing for Ba-La-Cu-Oxide materials. The designation "BLCO 21 -- II," etc. in the box in the right hand corner of this page and the designation "BLCO 2 I" in the circle in the middle of the page were the designations on the sample boxes in which the samples were located. I copied these designations directly into my notebook. On the bottom right hand corner of this exhibit, the words "dewar pumped  $3 \times 10^{-5}$  Torr 11/9/86" is indicated. I made this notation on November 9, 1986 indicating that the dewar was being pumped down in order to enable the resistivity versus temperature measurements to be made. Because this dewar leaked, the actual measurements had to be made within several hours of the pump-down.

6. The individual superconducting samples were attached to a long probe and slowly lowered into the liquid helium dewar while a current was passed through the sample and the voltage across two of the terminals measured. Sung Il Park assisted me. These measurements were recorded directly on an xy recorder which plotted resistivity versus temperature for these superconducting samples. These plots indicated an onset of superconductivity at about approximately 35K, and confirmed the results of Bednorz and Mueller in Switzerland. As an example, referring to the sample BLCO 2 having connecting wires 20, 21, 22 and 8, electrical current was applied between wires 20 and 8, while voltage measurements were made across the sample using contact terminals 21 and 22. Since the voltage is a function of the resistance of the material, by making the voltage measurements at constant currents, resistivity versus temperature plots can be developed. These resistivity versus temperature plots appear to be missing at this time. I believe that they may have been inadvertently thrown away when the laboratory was subsequently extensively cleaned.

7. During my measurement of the superconducting samples described hereinabove, Bradford G. Orr, who was a Post-doctoral employee

at the Research Center, came into my lab and observed these measurements, as did Albert M. Torressen. These measurements confirmed the high temperature superconductivity of these materials and I was enthusiastic about the results. I expressed my enthusiasm to Richard Greene, who was anxious to do specific heat measurements on these samples. Subsequent to my confirmation of their resistivity versus temperature measurements, I contacted Mueller in Zurich to inform him of my successful resistivity versus temperature measurements. In addition, I told several people about my laboratory measurements, including Arthur Williams, Alex Malozemoff, Paul Horn, and Praveen Chaudhari, all of whom work in the Thomas J. Watson Research Center.

8. From the time we received the superconducting samples in October, 1986 to the present, I, Richard Greene and Sung Il Park have worked on a daily basis to further explore and develop this technology. In particular, I observed Greene working on a daily basis to conduct specific heat measurements during November and December, 1986.

9. All acts described hereinabove relating to sample preparation, measurement and discussions of these measurements occurred in the United States.

10. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

*Chang C. Tsuei*

CHANG C. TSUEI

DATE: 3/30/88

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Teleprinter: ITPS CODE ZRL

ACTIVITY REPORT  
MAY-JUNE, 1986

August 15, 1986

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MATERIAL SCIENCE T. Schneider, Mgr.

SURFACE & MATERIAL SCIENCES E. Courtens, Mgr., Project 4181

#### Novel Research

##### Possible High-T<sub>c</sub> Superconductivity in the Ba-La-Cu-O System

J.G. Bednorz and K.A. Müller (Project 4196)

We observed a steep decrease of resistivity in sintered Ba-La-Cu-oxide samples, with the highest temperature of the onset in the 35 K range (Fig. 1).

The Ba-La-Cu-O system exhibits a number of oxygen deficient phases with perovskite-like layer-type structures. These are characterized by mixed-valent copper ions ( $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ ) and itinerant electronic states. In addition one expects polaron formation induced by the strong Jahn-Teller effect of  $\text{Cu}^{2+}$  in an octahedral oxygen environment. Thus our Ba-La-Cu-O system was anticipated to have considerable electron-phonon coupling and metallic conductivity.

Compounds with the composition  $\text{Ba}(x)\text{La}(5-x)\text{Cu}(5)\text{O}(5[3-y])$  have been prepared in polycrystalline form. Samples with  $x < 0.2$  and  $y > 0$ , annealed below  $900^\circ\text{C}$  under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound with  $\text{K}_2\text{NiF}_4$  type structure. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally a steep decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 35 K range. It is markedly reduced by high current densities (Fig. 1). The slow sensitivity decay towards low temperatures might possibly result from 2D superconducting fluctuations of perovskite layers of one of the phases present.

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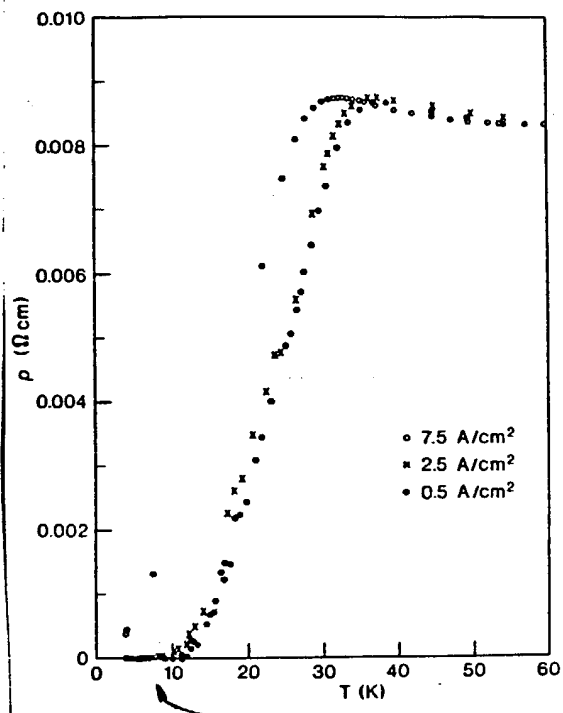


FIG. 1

$$0.008 \times 10^6 \mu\Omega \text{ cm}$$

$$\times \frac{1}{1000} = 8 \mu\Omega \text{ cm}$$

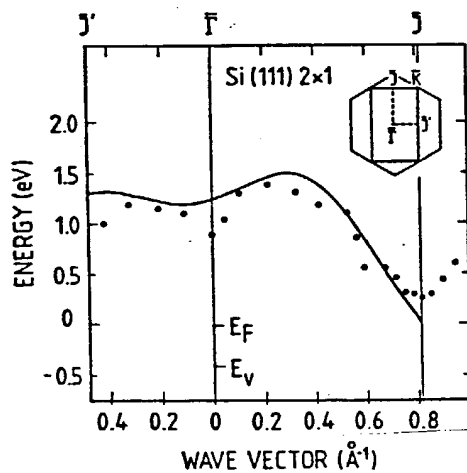


FIG. 2

## Possible High $T_c$ Superconductivity in the Ba-La-Cu-O System

J.G. Bednorz and K.A. Müller  
IBM Zürich Research Laboratory, Rüschlikon

Received April 17, 1986

CCT  
ExhB

Metallic, oxygen-deficient compounds in the Ba-La-Cu-O system, with the composition  $\text{Ba}_x\text{La}_{1-x}\text{Cu}_y\text{O}_{5(1-y)}$  have been prepared in the form of thin films. Samples with  $x=1$  and  $0.75$ ,  $y>0$ , annealed below  $900^\circ\text{C}$  under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, but possibly also from  $2D$  superconducting fluctuations of double perovskite layers of one of the phases present.

### 1. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of  $A15$  ( $\text{Nb}_3\text{Sn}$ ) and  $B1$  ( $\text{NbN}$ ) structure have so far shown the highest superconducting transition temperatures. Among many  $A15$  compounds, careful optimization of Nb-Ge thin films near the stoichiometric composition of  $\text{Nb}_3\text{Ge}$  by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest  $T_c = 23.3$  K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high  $T_c$ 's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li-Ti-O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high  $T_c$  [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations,  $n$ . In Nb-doped  $\text{SrTiO}_3$ , with  $n = 2 \times 10^{20} \text{ cm}^{-3}$ , the plasma edge is below the highest optical phonon, which is therefore unshielded

[6]. This large electron-phonon coupling allows a  $T_c$  of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  by Sleight et al., also a decade ago [8]. The highest  $T_c$  in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carriers  $n = 2-4 \times 10^{21} \text{ cm}^{-3}$  [9]. Flat electronic bands and a strong breathing mode with a phonon feature near  $100 \text{ cm}^{-1}$ , whose intensity is proportional to  $T_c$ , exist [10]. This last example indicates that within the BCS mechanism, one may find still higher  $T_c$ 's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in octahedral oxygen environment



show strong Jahn-Teller (J.T.) effects [13]. While  $\text{SrFe(VI)O}_3$  is a distorted perovskite insulator,  $\text{LaNi(III)O}_3$  is a J.T. undistorted metal in which the transfer energy  $b_\pi$  of the J.T.  $e_g$  electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba-La-Cu-O system. This system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T.  $\text{Cu}^{3+}$  and the J.T.  $\text{Cu}^{2+}$  ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

## II. Experimental

### 1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECPURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 5 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

### 2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIE-MENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2 $\theta$ ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the  $\text{K}_2\text{NiF}_4$  structure ( $a=3.79$  Å and  $c=13.21$  Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller  $x(\text{Ba})$ . The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite ( $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$ ) as described by Michel and Raveau [16].

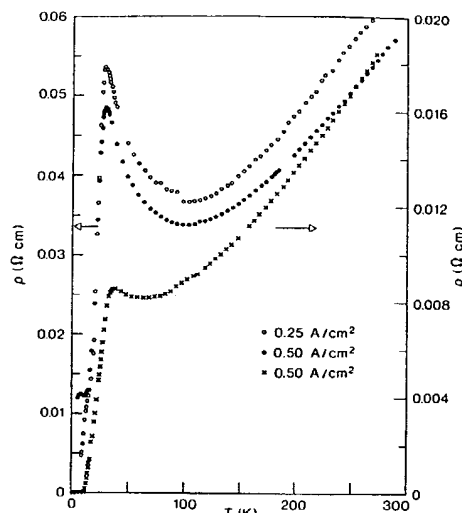


Fig. 1. Temperature dependence of resistivity in  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_3\text{O}_{5(1-x)}$  for samples with  $x(\text{Ba})=1$  (upper curves, left scale) and  $x(\text{Ba})=0.75$  (lower curve, right scale). The first two cases also show the influence of current density

### 3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by In wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Heraeus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with  $x(\text{Ba}) \leq 1.0$ , the conductivity measurements, involving typical current densities of 0.5 A/cm<sup>2</sup>, generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (> 90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and  $\text{O}_2$  partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted

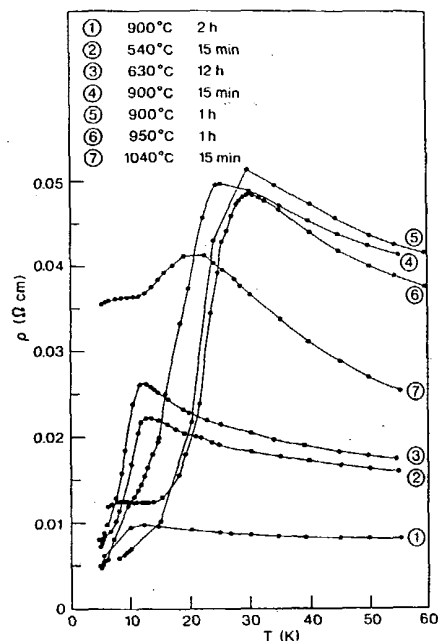


Fig. 2. Low-temperature resistivity of samples with  $x(\text{Ba})=1.0$ , annealed at  $\text{O}_2$  partial pressure of 0.2 bar (curve ①) and  $0.2 \times 10^{-4}$  bar (curves ② to ⑦)

towards the 30 K region. Curves ④ and ⑤, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve ④. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

### III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li-Ti-O system, and in superconducting

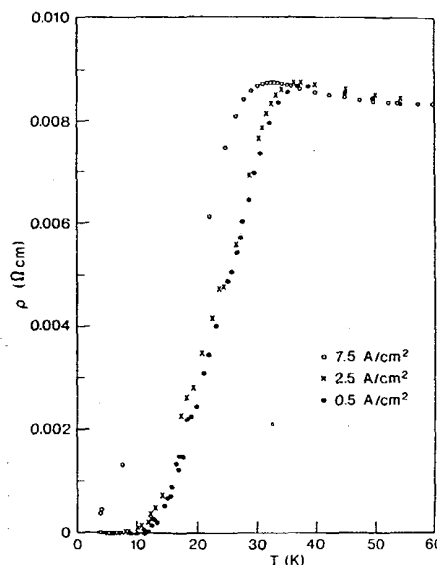


Fig. 3. Low-temperature resistivity of a sample with  $x(\text{Ba})=0.75$ , recorded for different current densities

$\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of  $\rho(T)$ , then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in  $\rho(T)$  with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li-Ti-O [5] or in our Ba-La-Cu-O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba-La-Cu-O phases exhibits this behaviour. Therefore, under the above premises, the peak in  $\rho(T)$  at 35 K, observed for an  $x(\text{Ba})=0.75$  (Fig. 1), has

to be identified as the start to superconductive cooperative phenomena in the isolated grains. It should be noted that in granular Al, Cooper pairs in coupled grains have been shown to exist already at a point where  $\rho(T)$  upon cooling has decreased by only 20% of its highest value. This has been proven qualitatively [19] and more recently also quantitatively [20] by the negative frequency shift occurring in a microwave cavity. In 100 Å films, a shoulder in the frequency shift owing to 2D fluctuations was observed above the  $T_c$  of the grains. In our Ba—La—Cu—O system, a series of layer-like phases with considerable variety in compositions are known to exist [16, 21], and therefore 2D correlations can be present.

The granularity of our system can be justified from the structural information, and more quantitatively from the normal conductivity behaviour. From the former, we know that more than one phase is present and the question arises how large are the grains. This can be inferred from the logarithmic fingerprint in resistivity. Such logarithmic increases are usually associated with beginning of localization. A most recent example is the Anderson transition in granular Sn films [22]. Common for the granular Sn and our samples is also the resistivity at 300 K, lying in the range of 0.06 to 0.02  $\Omega\text{cm}$ , which is near the microscopic critical resistivity of  $\rho_c = 10 L_0 h/e^2$  for localization. From the latter formula, an interatomic distance  $L_0$  in the range of 100 Å is computed, thus a size of superconducting grains of this order of magnitude must be present. Upon cooling below  $T_c$ , Josephson junctions between the grains phase-lock progressively [23] and the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2 (Fig. 1). At larger current densities, the weaker Josephson junctions switch to normal resistivity, resulting in a temperature shift of the drop, as shown in Fig. 3. The plateau in resistivity occurring below the 80% drop (Fig. 1) for the higher current density of 0.5 A/cm<sup>2</sup>, and Fig. 2 curve ⑥) may be ascribed to switching of junctions to the normal state.

The way the samples have been prepared seems to be of crucial importance: Michel et al. [21] obtained a single-phase perovskite by mixing the oxides of La and Cu and BaCO<sub>3</sub> in an appropriate ratio and subsequent annealing at 1,000 °C in air. We also applied this annealing condition to one of our samples, obtained by the decomposition of the corresponding oxalates, and found no superconductivity. Thus, the preparation from the oxalates and annealing below 950 °C are necessary to obtain a non-perovskite-type phase with a limited temperature range of stability exhibiting this new behaviour. The formation of this phase at comparatively low temperatures is favoured by the intimate mixture of the compo-

nents and the high reactivity of the oxalates owing to the evolution of large amounts of H<sub>2</sub>O and CO<sub>2</sub> during decomposition.

#### IV. Conclusion

In the concentration range investigated, compounds of the Ba—La—Cu—O system are metallic at high temperatures, and exhibit a tendency towards localization upon cooling. Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K. The system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress. An identification of that phase may allow growing of single crystals for studying the Meissner effect, and collecting specific-heat data to prove the presence of high  $T_c$  bulk superconductivity.

The authors would like to thank H.E. Weibel for his help in getting familiar with the conductivity measurement system, E. Courtens and H. Thomas for discussions and a critical reading of the manuscript.

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#### Note Added in Proof

Chemical analysis of the bulk composition of our samples revealed a deviation from the ideal La/Ba ratios of 4 and 5.66. The actual ratios are 16 and 18, respectively. This is in agreement with an identification of the third phase as CuO.

June 1985 -

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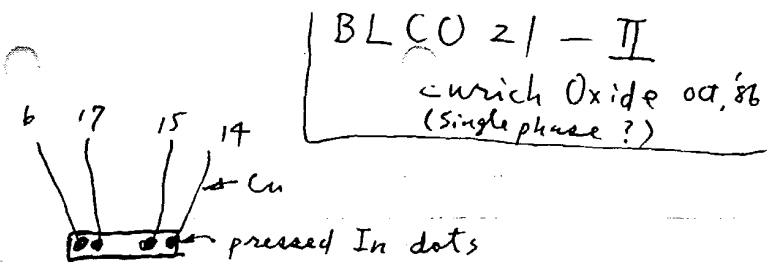
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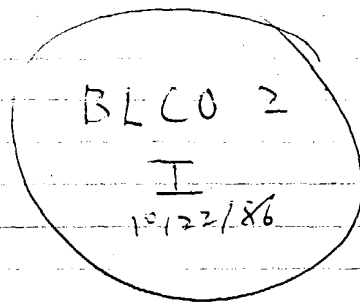
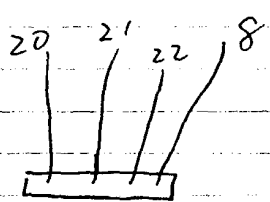
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 29, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF SUNG IL PARK  
WITH RESPECT TO HIGH  $T_c$  SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Sung Il Park, hereby declare and say that:

1. I received a PhD in Applied Physics from Stanford University in October, 1986. I joined the Thomas J. Watson Research Center of IBM Corporation in Yorktown, N.Y. on approximately October 20, 1986, and began work as a Post-doctoral employee. My initial assignment was in the areas of Thin Film Interfaces and high  $T_c$  superconductivity. Almost from the beginning of my employment by IBM Corporation I worked exclusively on high  $T_c$  superconductivity and reported to Chang C. Tsuei. I am presently working in the same capacity for Chang C. Tsuei, one hundred percent of my time being spent on high  $T_c$  superconductivity.

2. I was told by Chang C. Tsuei that superconducting samples had been received by Richard Greene, the samples having been brought from IBM Corporation's Research Lab in Zurich, Switzerland. These were said to be Ba-La-Cu-Oxides that had been fabricated by Georg Bednorz and Alex Mueller in Zurich, Switzerland and transported to the U.S. by Praveen Chaudhari. Soon after I began working for Chang C. Tsuei, he asked me to prepare two of these samples for measurements of resistivity versus temperature. To do so, I and Greene cut pieces from these samples to be used for the measurements. I then pressed indium dots into these cut samples to provide electrical contacts. I attached copper wires

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to the indium dots in order to allow connections to a current source and to voltage-measuring equipment. The individual copper wires were given number designations to allow them to be properly attached to the equipment used for the current and voltage measurements. This numbering system is represented by the two figures appearing in Chang C. Tsuei's laboratory notebook, a true copy of two pages of which are attached hereto and labeled Exhibit A.

3. In order to determine resistivity versus temperature, measurements were made of the current flowing through the Ba-La-Cu-Oxide sample while the voltage across two of the copper leads was measured. Both positive and negative polarity currents were used in order to avoid thermal effects that sometimes occur when making DC measurements. The superconducting sample was located on the end of a long probe and placed in a dewar containing liquid helium. The temperature was varied by using a heater placed near the sample. Data of current and voltage were taken from 4.2K to 50K. A germanium thermometer near the sample was used to measure the sample temperature. Since resistance is proportional to voltage, the voltage and current measurements allowed the resistance (and therefore the resistivity for a sample of known dimensions) to be measured as a function of temperature. I worked with Chang C. Tsuei to take these measurements and used a xy recorder to provide graphical plots of resistivity versus temperature for the temperature range 50K-4.2K for at least two of these Ba-La-Cu-Oxide samples.

4. The preparation and measurement of the aforementioned superconducting samples occurred at a date prior to November 15, 1986, and to the best of my recollection occurred on or about November 9, 1986, the date when a helium dewar was pumped down preparatory to taking the actual measurements. I believe that while I was assisting Chang C. Tsuei and working under his direction, Bradford Orr observed our data and graphical plots, and we told him the nature of the superconducting samples and the types of measurements that we were making.

5. My recollection of the dates when the preparation and measurement of these samples occurred is vivid to me. My first week of employment under Chang C. Tsuei was spent looking for an apartment and, upon beginning laboratory work the following week (about October 28, 1986), I was instructed by Chang C. Tsuei to immediately measure the



aforementioned samples. I cut pieces from these samples using a fine wire cutter following the direction of Richard Greene. This was done on or about October 28, 1986. After this I contacted the samples with indium as described above. This technique was very familiar to me as I had used indium contacts many times at Stanford University.

6. Both Chang C. Tsuei and I were enthused about our measurement results, as the data showed a superconducting onset temperature of about 35K followed by a drop to zero DC resistivity. We noted that the transition to zero resistivity was fairly wide, which we expected to be the case for samples that may have been unperfected and not of a single phase. In fact, the question of whether multiple phases were present in the material was something that was noted by Tsuei in the aforementioned laboratory notebook, identified as Exhibit A, attached hereto.

7. At this time, I have been unable to locate the actual data and graphical plots of resistivity versus temperature described hereinabove. I believe that this data may have been misplaced or inadvertently thrown out during an extensive cleaning of the laboratory. However, my memory of the events preparing the samples for measurements, performing the measurements and recording the data, and the results indicated by that data, are very clear in my mind.

8. All of the acts described in paragraphs 1 - 7 above occurred in the United States.

9. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

  
SUNG IL PARK

DATE: 3/30/88

June 85 -

VII

IBM  
YORKTOWN  
PATENT  
DEPARTMENT  
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# university note book



NAME W. Kately + C.C. Tsuei

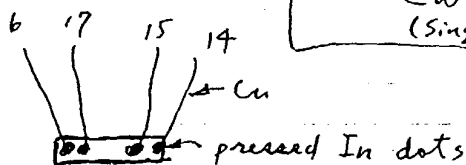
SUBJECT Low temp. T.C.

No. 06-9504 (S-1870-CM) • 11 IN. x 8½ IN. (28 cm x 21.6 cm) • 50 SHEETS • COLLEGE & MARGIN RULED

VERNON McMILLAN, Inc. ELIZABETH, N.J. 07208

A2

\*4

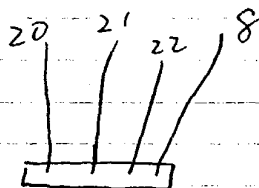


BLCU 21 - II

Zurich Oxide Oct '86  
(Single phase?)

B2

\*5



BLCU 2

I  
10/22/86

device pumped to  
 $3 \times 10^{-5}$  Torr 11/1/86

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March , 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF ALEXIS P. MALOZEMOFF  
WITH RESPECT TO HIGH T<sub>c</sub> SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Alexis P. Malozemoff, hereby declare and say that:

1. I have a PhD from Stanford University and was a Senior Manager in the Physical Sciences Department at the Thomas J. Watson Research Center of IBM Corporation at Yorktown, N.Y. in the fall of 1986. At that time, Chang C. Tsuei reported to me while Richard Greene and Sung Il Park reported to Chang Tsuei. I had general responsibility for a research program in superconductivity and amorphous materials.

2. In approximately September - October 1986, I was made aware of the pioneering work in superconductivity done by Bednorz and Mueller in Zurich. I had seen an activity report prepared by the Zurich Research lab of IBM Corporation, which detailed that work and the measurements that Bednorz and Mueller had made on Ba-La-Cu-O ceramic superconductors. In response, I discussed specific heat measurements that could be made on these superconducting materials to complement the work being done at Zurich by Bednorz and Mueller. My discussion was with Richard Greene whom I encouraged to be involved in this technical activity.

3. On or about November 15, 1986, Richard Greene and I traveled to Baltimore for a Magnetism conference. During our travel to Baltimore, we discussed Greene's ongoing experiments on high T<sub>c</sub> superconducting samples

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which he said had been received from Bednorz and Mueller. Specifically, we discussed Greene's preliminary data on specific heat measurements. Richard Greene reported to me that the diamagnetic signal was present but very small. I encouraged him to continue with his measurements with the anticipation that he might be able to present a paper at the Materials Research Society meeting that was scheduled for December, 1986.

4. I recall Chang Tsuei telling me his measurements of resistivity versus temperature on the superconducting samples of Ba-La-Cu-Oxides which had been obtained from Zurich. These measurements were done at the aforementioned Research Center and Tsuei reported that his measurements confirmed earlier measurements of Bednorz and Mueller and were consistent with the results published by Bednorz and Mueller in Z. Phys. B-Condensed Matter 64, pp. 189-193 (1986). My recollection of the exact date Chang Tsuei told me of his resistivity versus temperature measurements is not clear. However, I do know that he told me in either November or December of 1986. To the best of my recollection, Tsuei's discussion with me was shortly after the Materials Research Society meeting in Boston the first week of December, 1986.

5. I do have a strong recollection of the work of Richard Greene on the specific heat measurements of these samples and of his measurements of resistivity versus temperature in the presence of a magnetic field. Greene's work at the Research Center started soon after he received the superconducting samples in October, 1986 and continued on a daily basis throughout the remainder of 1986 and into 1987. He discussed with me and showed me data concerning these measurements, which indicated to me that a portion of the samples was superconducting. During this time he told me that he also communicated regularly with Bednorz and Mueller in Zurich to inform them of his work and to coordinate his efforts with those of Bednorz and Mueller. He said that he received technical guidance and support from Bednorz and Mueller and worked in complete collaboration with these individuals.

6. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made in the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March , 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF PAUL M. HORN  
WITH RESPECT TO HIGH T<sub>c</sub> SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Paul M. Horn, hereby declare and say that:

1. I am employed in the Thomas J. Watson Research Center of IBM Corporation at Yorktown, N.Y., where I am acting Director of the Physical Sciences Department. I received a PhD in Physics in 1973 from the University of Rochester.

2. In approximately November, 1986, I recall a conversation in which Chang C. Tsuei told me of measurements that he had recently done on samples of high T<sub>c</sub> superconducting materials which he said were received from J.G. Bednorz and K.A. Mueller, of Zurich, Switzerland. These were described as samples of the type described by Bednorz and Mueller in Z. Phys. B-Condensed Matter 64, pp. 189-193 (1986), i.e., superconducting copper oxide materials in the system La-Ba-Cu-O.

3. I recall my discussion with Chang C. Tsuei because he was quite excited about his measurements and explained to me that they were "very recent measurements" of resistivity versus temperature that he had made on these samples. I recall that Tsuei told me that the onset temperature for superconductivity was in the mid-thirty K range. Tsuei told me that the samples superconducting and that his results looked like the results published by Bednorz and Mueller in the Z. Phys. B.

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article mentioned hereinabove.

4. I do not recall seeing Chang Tsuei's actual data measurements, but was independently aware that the superconducting samples that he used were obtained from Bednorz and Mueller and I was familiar with the general composition of these superconducting samples.

5. All acts described hereinabove occurred in the United States, with the exception of the laboratory work of Bednorz and Mueller, which was performed in Zurich, Switzerland.

6. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Paul M. Horn  
PAUL M. HORN

DATE: 3/30/88

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL. : Date: March 29, 1988  
Filed: 05/22/87 : Serial No.: 06/053,307  
Group Art Unit: 115 : Examiner: Dennis Albrecht  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION

DECLARATION OF CHENG-CHUNG JOHN CHI  
WITH RESPECT TO HIGH T<sub>c</sub> SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Cheng-Chung John Chi, hereby declare and say the following:

1. I have a PhD in Physics which I received from the University of Pennsylvania in 1976. After graduation, I did Post-doctoral work at the University of California, Berkeley and then joined the Research Division of IBM Corporation in 1979. I am presently a research staff member on the technical staff of the Director of Research at the Thomas J. Watson Research Center of IBM Corporation located at Yorktown, New York.

2. At a time prior to approximately the middle of November, 1986, Chang C. Tsuei told me of measurements he made on samples of high T<sub>c</sub> superconducting material which he said were received from Georg Bednorz and K. A. Mueller, two physicists working for IBM Corporation in Zurich, Switzerland. These samples of superconducting material were La-Ba-Cu-O crystalline materials of the type described by Bednorz and Mueller in Z. Phys. B-Condensed Matter 64, pp. 189-193 (1986). Chang Tsuei said that he had measured resistivity versus temperature of these samples.

3. In the time frame mentioned hereinabove, Chang Tsuei showed me plots of resistivity versus temperature for the measurements he had made on these superconducting samples. I recall him telling me that the superconducting transition was "not really sharp", which is to

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be expected for samples prepared during the infancy of a technology development. I recognized that these plots were evidence of superconductivity with high  $T_c$ , even if the transition were not very sharp at that time. Based on Tsuei's statements to me, I believe that these resistivity versus temperature plots were shown to me within a day or two of the time Tsuei made these measurements in his laboratory.

4. All acts described by me in this declaration occurred in the United States.

5. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Cheng-Chung John Chi  
CHENG-CHUNG JOHN CHI

DATE: 3/30/88

IN THE U.S. PATENT AND TRADEMARK OFFICE

APPLICANT: J. G. BEDNORZ ET AL      DATE: DECEMBER 29, 1987  
SERIAL NO.: 06/053,307      GROUP ART UNIT: 115  
FILING DATE: 05/22/87      EXAMINER: DENNIS ALBRECHT  
FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE,  
AND METHODS FOR THEIR USE AND PREPARATION  
TO: The Commissioner of Patents and  
Trademarks  
Washington, D. C. 20231

PETITION FOR SUSPENSION OF ACTION UNDER 37 CFR 1.103

Applicants respectfully request the Commissioner of Patents and Trademarks to suspend action by the Patent Office on the subject application until March 7, 1988. The fee (\$72.00) for this petition may be charged to Deposit Account No. 09-0468.

In summary, the reason for this request is that the undersigned requires this period of time in order to provide information previously requested by the Examiner as a result of his preliminary review of this application. The information to be provided relates to acts of invention in the United States, where the conception and reduction of practice are based on an idea first conceived and reduced to practice in Switzerland. Evidence of conception and reduction to practice in the United States involves detailed interviews with

at least 12-15 individuals, many of whom are unavailable. In particular, the inventors are the 1987 Nobel Prize winners in Physics, whose residences are in Europe and whose schedules render their availability extremely limited. This information will be provided to the Patent and Trademark Office in order to overcome potential 35 USC 102(a) references, the provision of which will eliminate considerable unnecessary effort on the part of the examiner and which will expedite prosecution. A more detailed basis for the foregoing petition will now be provided.

#### BACKGROUND

1. The invention concerns the breakthrough discovery of K.A. Mueller and J.G. Bednorz relating to high temperature superconductivity. The inventors received the 1987 Nobel Prize in Physics for this accomplishment, which was followed by worldwide acclaim and efforts to further their concept in superconductor technology.
2. Inventors Bednorz and Mueller first published their initial discovery of superconductivity at high temperatures in September, 1986 in Z. Phys. B, 64, page 189. Subsequent to that first publication, the inventors have au-

thored additional publications, as have many researchers in this field.

3. Because a patent application based on the discoveries described in the aforementioned Z. Phys. B reference was not filed prior to that publication, the subject patent application was filed in the United States based on the allowed one year grace period from the date of publication (Sept. 1986) of this first article. Because there have been intervening publications of others subsequent to the initial publication by the inventors but prior to the date of filing of the subject patent application, an office action based on 35 USC 102 can be prepared by the examiner. However, applicants can and will establish completion of their invention in the United States prior to the date of any of these intervening publications, all of which acknowledge the discovery by the present inventors. In order to eliminate undue effort and expenditure of funds, the subject petition is being filed.

4. Applicants can and will show acts attributable to them, consistent with the discovery described in the aforementioned publication in Z. Phys. B., were made in this country prior to any publication by others who began working in high  $T_c$  superconductivity after the Sept. 1986

publication of the present inventors. This evidence will include introduction into the United States of samples of superconducting material prepared by the inventors and tested in a manner consistent with the acts first described in the Z. Phys. B. article. This work first occurred in the United States at the Yorktown Heights, N. Y. research laboratory of the present assignee, where work continued on a daily basis to reproduce the acts originally accomplished by the inventors in Switzerland, as well as additional acts evidencing superconductivity in these samples.

5. In order to establish completion of the invention in the United States, it is necessary to interview 12-15 individuals, and to locate large volumes of data contained in various notebooks and laboratory progress logs. Many of the people sought to be interviewed have been unavailable and remain unavailable at this time. In particular, the inventors have a schedule which takes them around the world for speaking engagements and other activities based on their celebrity status. I have been informed that they will not be available for further discussions with me until approximately the first week in February, which makes it difficult to quickly com-

plete, review and have executed the papers necessary to establish the required acts in the United States.

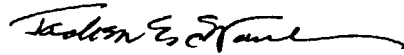
6. Because the prosecution of this application will require the provision of this information and further because this is the basic patent application in this technology, it is believed that suspension of any office action to allow the filing of these papers is in the best interest of the patent office, the public, and the inventors. Every effort is being made to expedite and organize the material which will be presented so as to make it as clear and self-explanatory as possible. It is further believed that prosecution of all other applications in the field of high temperature superconductivity will depend to some degree on the prosecution of the subject application, thereby providing another reason to suspend prosecution until the aforementioned information is filed in the patent office.

The undersigned has conducted preliminary interviews with approximately 8 of the individuals required to be interviewed in order to provide the necessary information, and is diligently attempting to provide interview schedules with the other individuals. The data and the various activities described by each will have to be coordinated together with the

laboratory data, charts, plots, etc. evidencing the large amount of activity that was undertaken in 1986 in the United States by others together with and on behalf of the inventors. For this reason, the present request is made.

Respectfully submitted,

J.G. BEDNORZ ET AL



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Yorktown Heights, N. Y. 10598